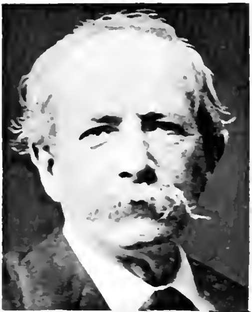
EXPLOSIVES

VOLUME II



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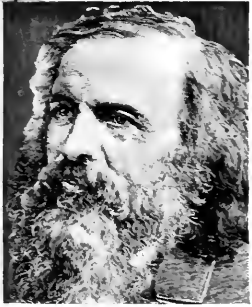

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EXPLOSIVES

BY

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SECOND EDITION

Vol. II

PROPERTIES AND TESTS

WITH 80 ILLUSTRATIONS

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LIST OF PRINCIPAL ABBREVIATIONS

JOURNALS, ETC.

A. and E.	*Arms and Explosives.*
Ang.	*Zeitschrift für angewandte Chemie.*
A.R.	*Annual Reports of H.M. Inspectors of Explosives.*
Ber.	*Berichte of the German Chemical Society.*
Bull.	*Bulletin of U.S. Bureau of Mines.*
Chem. Ind.	*Die chemische Industrie.*
Chem. Trade J.	*Chemical Trade Journal.*
Compt. rend.	*Comptes Rendus.*
C.Z.	*Chemiker-Zeitung.*
J Soc. Chem. Ind.	*Journal of the Society of Chemical Industry.*
P. et S.	*Mémorial des Poudres et Salpêtres.*
Phil. Trans.	*Philosophical Transactions of the Royal Society.*
Proc. R.S.	*Proceedings of the Royal Society.*
S.R.	*Special Reports of H.M. Inspectors of Explosives.*
S.S.	*Zeitschrift für das gesamte Schies- und Sprengstoffwesen.*
Trans. Chem. Soc.	*Transactions of the Chemical Society.*

BOOKS

Chalon.	*Les Explosifs Modernes.*
Cundill and Thomson.	*Dictionary of Explosives.*
Hime.	*Gunpowder and Ammunition*, by Lieut.-Colonel Hime.
Manufacture.	*The Manufacture of Explosives*, by O. Guttmann.
Monumenta.	*Monumenta Pulveris Pyrii*, by O. Guttmann.
Twenty Years' Progress.	*Twenty Years' Progress in Explosives*, by O. Guttmann.
Rise and Progress.	*The Rise and Progress of the British Explosives Industry.*
Worden.	*The Nitro-cellulose Industry*, by Worden.
Zschokke.	*Militarische Spengtecknik*, by B. Zschokke.
Vennin et Chesneau.	*Les Poudres et Explosifs*, 1914.

OTHER ABBREVIATIONS

b.p.	boiling-point.	G/c.	guncotton.
c.c.	cubic centimetres.	m.p.	Melting-point.
coll. cot.	collodion cotton.	N/c.	Nitro-cellulose.
D/n/g.	dinitroglycerine.	N/g.	Nitro-glycerine.
D/n/t.	dinitrotoluene.	sp. gr.	Specific gravity.
g.	grammes.	T/n/t.	Trinitrotoluene.

Temperatures are always in degrees Centigrade unless otherwise stated.

PART IX

PROPERTIES OF EXPLOSIVES

CHAPTER XXVIII

PHYSICAL CHARACTERS AND TESTS

External examination : Colour : Density : Flashing test : Shaking test : Absorption of moisture : Deliquescence : Exudation : Test for liquefaction : Wrappers : Pressure test : Keeping test : Centrifugal test : Sensitiveness and danger in handling : Friction test : Falling weight test : Sensitiveness to detonation : Effect of temperature : Transmission of detonation : Sensitiveness to heat : Temperature of ignition : Time of ignition : Tests of International Committee : British classification

External Examination

The external examination of an explosive comprises the observation of its general appearance and character. In the case of black powders the lustre, hardness, shape and size of the grains are all matters of importance. The size of the grains is determined by sifting a known weight through a series of sieves and ascertaining what proportions pass through the different meshes.

At the American Bureau of Mines the following characteristics of blasting explosives are noted :

1. Granulation. Structure : (*a*) granular, (*b*) fibrous, (*c*) powdered. Size : (*a*) very fine, (*b*) fine, (*c*) coarse, (*d*) very coarse.

2. Liquidness : (*a*) very wet, (*b*) wet, (*c*) dry, (*d*) very dry.

3. Hardness : (*a*) very hard, (*b*) hard, (*c*) soft, (*d*) very soft.

4. Cohesiveness : (*a*) very cohesive, (*b*) moderately cohesive, (*c*) slightly cohesive, (*d*) not cohesive.

Colour. According to Benjamin [1] the colour may be measured by means of a Maxwell rotating disc. A circular brass plate 29 cm. in diameter is mounted so that it can be rotated, and on it are placed the various colour discs, which have a diameter of 25 cm., and are held in place by means of a cover of celluloid. The colour discs are adjusted until on rotating the apparatus the colour exactly matches that of the explosive. The amount of the various constituents is then read off on a scale round the circumference of the brass disc, and the figures thus obtained serve to define the colour.

Density

Absolute specific gravity. The absolute specific gravity of an explosive may be ascertained by reducing it to a very fine state of division, introducing a known weight into a specific

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[1] *Eighth Int. Cong.*, vol. iv, p. 12.

gravity bottle, filling up with a liquid that has no action on the powder, removing all air under a vacuum pump, and weighing after bringing it to standard temperature in the usual way for the determination of the specific gravity of solids. This, however, is a determination that is seldom carried out, as the absolute specific gravity does not often require to be known for practical purposes, and it can be calculated with sufficient accuracy from the known specific gravities of the different constituents.

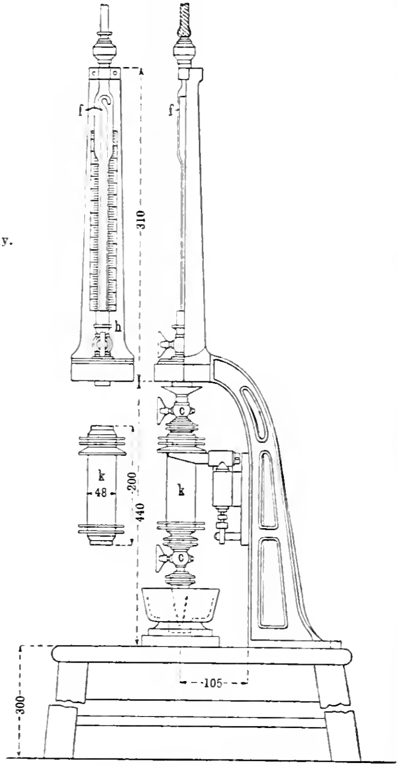

Fig. 79. Bianchi's Densimeter

Density.

By the density of an explosive is usually meant the density of the individual pieces or grains including any air there may be in the pores or interstices. It is determined by ascertaining the volume of some suitable medium that is displaced by a known weight of the explosive. This volume depends to some extent on how far the medium is caused to penetrate into the pores of the material. For black powder Bianchi's apparatus is generally used (Fig. 79), and the medium is mercury. It consists of a vessel, *k*, which can be screwed on to the apparatus so that the whole constitutes a sort of barometer. Two steel cocks screw on to *k*: the lower one has a tube drawn out to a point which dips into a basin of mercury, the upper one screws on to an upright tube, *f*, which has graduations. At either end of *k* there is a piece of fine iron wire gauze to prevent grains of powder escaping. One hundred grains of powder are weighed out into *k*, which is then connected up, and the air is pumped out through the top of *f* by means of a vacuum pump, until the mercury attains a steady level. The lower cock is then closed, the vacuum is broken so that the powder is under a certain head of mercury, then the upper cock is closed and *k* is disconnected and weighed. The mercury is then run out and the operations are repeated; the weight should then be the same. The mercury should be brought to a standard temperature before the determination and maintained at it. If S be the specific gravity of mercury at this temperature, and W the weight of the vessel filled with mercury alone, and W^1 the weight filled with powder and mercury, then the density of the powder is equal to

$$\frac{(W - W^1) + 100}{S \times 100}.$$

If the powder be of larger size than RLG² it is first broken up in a mortar and the dust is sifted out and discarded.

For moulded prismatic powders use is made of Bode's densimeter, in which the volume is ascertained by finding the weight required to immerse a prism below the surface of mercury. The calculation is much the same as with Bianchi's apparatus.

At the 8th International Congress Snelling described a densimeter (Fig. 80), which works somewhat on the same principle as the Bianchi, but does not require a vacuum pump, a Torricellian vacuum being formed by forcing mercury from the vessel e into a by means of water pressure, and then opening the waste cock x, so that

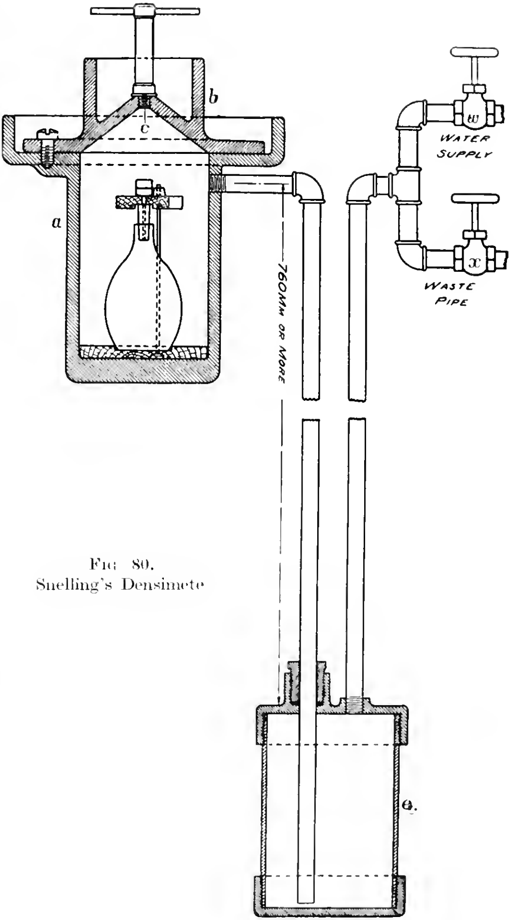

FIG. 80.
Snelling's Densimete

the pressure is relieved. The powder is weighed out into the pyknometer, which is clamped down inside a, and the lid b screwed on. The cock w is opened, so as to force the mercury into a, and the valve c is opened to allow the air to escape. When mercury commences to come through c, c and w are closed and x is opened, whereby a vacuum is formed in a. Then x is closed and w opened and the whole cycle of operations is repeated until no more air is removed through c. Then the pyknometer is taken out and weighed.

The densities of black powders found by these methods are usually within the limits 1·65 to 1·85, but the absolute specific gravity as calculated from those of its constituents is considerably higher; that of saltpetre is 2·08, of sulphur (rhombic) 2·05; that of charcoal depends upon the burning process and is difficult to determine on account of the pores, but it is at least 1·5 and may approach that of graphite 2·2. The absolute specific gravity of black powder is therefore at least 2·03, which shows that under the conditions of the density determinations, many pores in the interior of the grains do not become filled with mercury.

The density of high explosives may be ascertained by carefully measuring and weighing a cartridge, but in consequence of the irregular shape, this may not give a satisfactory result. The American Bureau of Mines determines it by weighing in sand. American 40 per cent. dynamite was thus found to have a density of 1·22 to 1·24. In Snelling's densimeter it gives results in the neighbourhood of 1·6, more nearly approaching the absolute specific gravity. The densities or "apparent specific gravities" of American safety explosives determined in sand varied from 0·84 to 1·54, those of European safety explosives from 0·68 to 1·36.

ravimetric ensity.

The gravimetric density of a charge in a fire-arm is the weight of the charge divided by the weight of water that would be required to fill the chamber space. As applied to gunpowders it is the weight that will fill unit volume of a vessel when simply poured in and very gently shaken down. In Belgium vessels of 1, 2 or 10 litres capacity are used according to the size of the grains.[1] Above the vessel is fixed a funnel of somewhat greater capacity closed below by a slide. After the funnel has been filled the slide is removed and the powder allowed to run into the vessel. By means of a straight-edge it is then struck off level with the rim and weighed. The following are the densities of some German naval powders:

		Density	Gravimetric Density
Rifle powder M 71	not under	1·655	0·915
New rifle powder M 71	,, ,,	1·755	0·945
Cannon powder		1·60	0·925
Large grain powder		1·66	0·970
,, ,, blasting powder		1·75	0·975

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[1] Gody, *Les Explosifs*, p. 146.

Vennin gives the following particulars about French black powders:[1]

Powder	Density	Gravimetric Density	Grains per Gramme	Sieves
Rifle F_3	1·740	·938–·942	900– 1,200	1·0–1·8 mm.
Sporting, ordinary, No. 0.	1·725	·940–·970	650– 950	1·2–1·6 mm.
,, ,, No. 1.	1·725	·940–·970	2,000– 3,000	0·8–1·2 mm.
,, ,, No. 2.	1·725	·960–·990	4,000– 6,000	No. 0–0·8 mm.
,, ,, No. 3.	1·725	·960–·990	8,000–12,000	No. 1–No. 0
,, strong, No. 1.	1·80	·960–·990	2,000– 3,000	0·8–1·2
,, ,, No. 2.	1·80	·960–·990	4,000– 6,000	No. 0–0·8 mm.
,, ,, No. 3.	1·80	·940–·970	8,000–12,000	No. 1–No. 0
,, ,, No. 4.	1·80	·940–·970	20,000–30,000	No. 5–No. 1

The difference between the gravimetric density and the ordinary density shows that there is almost as much free air space between the grains as is occupied by the grains themselves. Powders containing grains varying very much in size have higher gravimetric densities than those which are fairly uniform. Thus Snelling found a number of American blasting powders to have gravimetric densities from 1·09 to 1·20. There is no necessary connection between the ordinary and gravimetric densities.

The determination of the density of a gelatinized smokeless powder affords some indication of the quantity of ungelatinized nitro-cellulose it contains, and consequently of the porosity of the powder. According to de Mosenthal the absolute specific gravity of nitrocellulose is 1·65 to 1·68. The following have been given as the densities of some nitro-cellulose powders:

Poudre B. M.	1·52
American multiperforated	1·563
Spanish	1·55 to 1·58
Rottweil	1·60

Allowance must of course be made for the residual solvent and other substances contained in the powder. The density of cordite is 1·56 to 1·59.

FLASHING TEST

To ascertain whether they have been thoroughly incorporated black powders are submitted to the "flashing" test by burning them on a glass, porcelain or copper plate. The *Treatise on Service Explosives* gives the following instructions for carrying out the test: The powder is put into a small copper cylinder like a large thimble, which is then inverted on the flashing plate. This ensures that the grains of powder are arranged in much the same way each time, which is very important. If the powder has been thoroughly incorpor-

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[1] Vennin et Chesneau, *Poudres et Explosifs*, p. 335, etc.

ated, it will "flash" or puff off when touched with a hot iron with but few "lights" or sparks, and leaving only some smoke marks on the plate. A badly incorporated powder will give many sparks, and also leave specks of undecomposed saltpetre and sulphur forming a dirty residue. Although a very badly worked powder can be detected at once, it requires an experienced eye to form an accurate judgment of the comparative merits of ordinary powders; for if made from slack burnt charcoal, the powder will never flash so well as if the charcoal has been made at a high temperature. Powder which has once been injured by damp will flash very badly, no matter how carefully it has been incorporated. This is because the saltpetre has passed partially into solution and segregated into crystals of comparatively large size.

SHAKING TEST

The shaking test is applied to an explosive to ascertain whether it has been so incorporated that the constituents will not separate out under the ordinary conditions of transit and use. The German Railway Commission places 100 g. in a dry wide-mouthed bottle of 150 c.c. capacity, which is shaken backwards and forwards horizontally 150 times a minute for five hours.

A test which more nearly imitates the conditions of actual transit consists in jerking it up and down vertically. The powder is placed in a closed copper canister, which is fixed to the steel table of the shaking machine. This is raised a few mm. by means of a cam and then falls with a jerk on to an adjustable steel top. The apparatus can be provided with a counting arrangement, so that the number of falls is known. The separation of the ingredients, or other change in the explosive. may be seen in some cases by superficial examination. in other cases it may be necessary to apply tests for sensitiveness or other physical properties, or to make chemical analyses of portions from the top and bottom of the small canister.

ABSORPTION OF MOISTURE

Amorphous materials, such as charcoal, wood-meal, flour and nitro-cellulose take up moisture from the air in amounts depending upon the temperature and the degree of saturation of the atmosphere. Crystalline substances behave quite differently in this respect: if the pressure of water vapour be below a certain amount, varying with the different substances and with the temperature, no moisture is taken up. At a higher pressure of water vapour a compound with a fixed number of molecules of water may be formed; and when the pressure of water vapour in the air is higher than the vapour pressure of a saturated solution of the substance it deliquesces, gradually becoming entirely liquid.

ygrometric est. In the case of black powder it is important that it should not absorb moisture rapidly in a moist atmosphere, and so be rendered unserviceable. Powders are therefore submitted to the "hygrometric test": about 65 grammes are put into a little tray with a bottom of fine wire gauze, and placed inside a box containing a considerable quantity of a saturated solution of saltpetre. Powders of the smaller sizes are allowed to remain in the box twenty-four hours, the larger sizes forty-eight hours. The powder is then weighed again, and the percentage gain in weight together with the moisture originally present in the powder is the hygroscopicity. If the special apparatus here mentioned is not available the determination can be made in an ordinary desiccator containing a saturated solution of saltpetre mixed with crystals of the salt, and 2 to 5 g. can be weighed out on to a watch-glass. The results will be much the same.

Gunpowder made with charcoal carbonized at a low temperature absorbs moisture far more readily than that made with hard-burnt charcoal, but the absorption also depends very much on the purity of the saltpetre used for making the powder. If the saltpetre were absolutely pure, there would be practically no tendency for it to take up moisture from the saturated solution in the hygrometric box, but if there be a small proportion of a soluble impurity such as sodium chloride, there is tendency for a thin film of a solution saturated both with sodium chloride and potassium nitrate to be formed on the surface of each crystal. Such a solution has a much lower vapour pressure than that of a solution saturated with potassium nitrate only. Consequently, a very small proportion of sodium chloride will cause a great increase in the amount of moisture absorbed by the powder. Other soluble salts, such as sodium nitrate, have a similarly injurious effect. Even if a less soluble substance be mixed with the saltpetre, it will have a deleterious effect, because the solubility of two substances combined is nearly always greater than that of one alone. If the powder absorb sufficient water to make it moist, the grains will cake together, but a more serious effect is that the minute particles of ground saltpetre gradually coalesce into crystals of comparatively large size, and consequently even if the powder be dried again it will not regain its explosibility in full measure, unless it be worked again in a mill.

Deliquescence

The following Table shows the tendency of pure potassium nitrate to absorb moisture at different temperatures:

Temperature	Solubility	Relative Humidity
0°	13·3	97·0
10°	20·9	96·5
20°	31·6	94·7
25°	37·3	93·8
30°	45·8	92·5
40	63·9	90·0

In the middle column is given the number of parts by weight dissolved by 100 parts of water, and in the last column the amount of moisture in air in equilibrium with the saturated solution, the quantity of water vapour in air saturated with moisture from distilled water at the same temperature being taken as 100.

Blasting explosives frequently contain salts, such as the nitrates of sodium and ammonium, which are far more liable to deliquesce than potassium nitrate. It is useful to be able to express this property by a figure, and for this purpose the reduction of the vapour pressure of the saturated solution as compared with distilled water may be used, and in order to get a comparative figure, this may be divided by the corresponding reduction in the case of saltpetre at the same temperature. Unfortunately the vapour pressures of the saturated solutions at ordinary temperatures have been determined in practically no cases: but those of solutions of various strengths have been measured at different temperatures in the case of the most of the more important substances, and from these measurements the reduction of the vapour pressure in the case of the saturated solutions can be calculated, the solubilities being known. In the case of some organic substances, such as sugar, the reduction of the vapour pressure follows approximately Raoult's law, that is to say, the reduction of the vapour pressure is to the vapour pressure of pure water as the number of molecules of solute is to the sum of the numbers of molecules of solute and solvent. But inorganic salts, as a rule, reduce the vapour pressure by amounts considerably greater than those corresponding to Raoult's law. This is due partly to electrolytic dissociation, and partly to combination of the solute with the water. A factor can be obtained by which the figures corresponding to Raoult's law must be multiplied in order to obtain results giving approximately the reductions of vapour pressure caused by saturating water with the substances.

In the Table on page 420, where the factors are in brackets, there have been no data from which to calculate them, and they have been estimated from analogy with other similar substances. In many cases the figures are only very rough approximations, but for ordinary purposes they are near enough. Moreover, the deliquescence is affected so greatly by the presence of traces of impurities, that highly accurate estimations would not enable one to predict the behaviour when exposed to moist air with much greater accuracy. When an explosive contains two or more soluble substances mixed together, it is likely to be more deliquescent than if it only contained one of them. In the column of "relative humidity" is given the amount of moisture in air which is in equilibrium with the saturated solution, air saturated with water vapour being taken as 100. If the humidity of the air be less than this the pure substance will not deliquesce; if greater it will. This number subtracted from 100 and divided by the corresponding value for potassium nitrate gives the "relative deliquescence."

Any substance, which has a relative deliquescence above 3, requires to be stored under such conditions that moist air cannot obtain access to it. The cartridges of explosives containing nitrate of sodium or ammonium are therefore generally dipped into paraffin wax. As the ammonium salt is about twice as hygroscopic as the sodium compound, this precaution is specially necessary with the important class of explosives containing it. The French "Commission des Substances explosives" carried out experiments in which these salts, and mixtures of them, were exposed to atmospheres containing various amounts of water vapour:[1] the results are in accordance with the figures given in the table.

Explosives containing ammonium oxalate are no longer required in England to be enclosed in waterproofed inner packages.[2] This also is in accordance with the above calculations, which show that ammonium oxalate is one of the least deliquescent of the substances that are used in the manufacture of explosives; the danger is rather that efflorescence may occur.

Exudation

Explosives containing nitro-glycerine are liable under certain circumstances to sweat out some of this substance, and this is a source of serious danger. Kieselguhr dynamite, for instance, gives up practically the whole of its nitroglycerine if it becomes wet. If the guhr is over or under calcined, or if it be insufficiently absorbent, this tendency is much increased.

Gelatinized explosives are liable to become too liquid at a moderately high temperature, if the collodion cotton be of an unsuitable character, or if there be not enough of it. The Home Office prescribes that these explosives shall pass the following test:

Test for liquefaction.

A cylinder of length about equal to the diameter is cut from a cartridge, and the ends are cut flat. This is placed on end, without any wrapper, on a flat surface, and secured by a pin passing vertically through its centre. In this condition the clylinder is exposed to a temperature of 85° to 90° F. for 144 consecutive hours (six days and nights). During this exposure the cylinder must not diminish in height more than a quarter of its original height, and the upper cut surface must retain its flatness and the sharpness of its edge.

The German Railway Commission lays down that a complete cartridge shall be kept for five days at 30° C. (86° F.). No nitro-glycerine must exude, and after cooling the cartridge must be unchanged.

Wrappers.

In the case of one particular brand of gelatinized explosives its great tendency to exude was traced by Hake to the use of wrappers of parchment paper made from wood pulp.[3] Such paper in the process of parchmentizing with sulphuric acid develops pores through which the nitro-glycerine is drawn by capillary action and forms beads on the outside of the wrapper. Parchment paper made from cotton rags is free from this defect. In Germany wrappers of paraffined paper are used.

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[1] *P. et S.*, vol. xvi, 1912. p. 9.

[2] *A.R.*, 1910, p. 43.

[3] *J. Soc. Chem. Ind.*, 1905, p. 915.

Substance	Formula	Molecular Weight	Solubility g. per 100 g. water	Temperature	Factor	Relative Humidity	Relative Deliquescence KNO_3 = 1
Nitrates							
Ammonium	NH_4NO_3	80·0	153·4	12·2°	(1·3)	67·0	9·2
,,	,,	80·0	192·4	20·2°	(1·3)	60·0	7·6
Sodium	$NaNO_3$	85·0	80·6	10·0°	1·7	73·5	7·6
,,	,,	85·0	87·8	20·0°	1·7	72·8	5·1
Calcium	$Ca(NO_3)_2$	164·1	121·0	18·0°	3·27	62·0	7·8
Strontium	$Sr(NO_3)_2$	211·6	70·8	20·0°	2·53	86·0	2·7
Barium	$Ba(NO_3)_2$	261·4	9·2	20·0°	1·97	98·8	0·23
Copper	$Cu(NO_3)_2$	187·6	117·0	18·0°	(2·5)	75·0	5·1
Lead	$Pb(NO_3)_2$	331·2	52·3	17·0°	(2·0)	94·5	1·2
Chlorides							
Ammonium	NH_4Cl	53·5	35·2	15·0°	1·82	81·0	4·4
Potassium	KCl	74·6	32·4	15·0°	1·7	87·6	2·9
Sodium	$NaCl$	58·5	35·8	15·0°	2·49	76·0	5·5
Calcium	$CaCl_2$	111·0	74·5	20·0°	5·3	43·0	10·8
Mercuric	$HgCl_2$	271·5	5·4	20·0°	(3·0)	98·9	0·20
Chlorates							
Potassium	$KClO_3$	122·6	7·2	20·0°	1·16	98·8	0·23
Sodium	$NaClO_3$	106·5	89·3	12·0°	2·3	70·0	7·7
Perchlorates							
Ammonium	NH_4ClO_4	117·5	20·0	(15·0°)	(1·5)	95·6	1·0
Potassium	$KClO_4$	138·6	1·2	15·0°	1·6	99·8	0·06
Sulphates							
Ammonium	$(NH_4)_2SO_4$	132·1	74·2	15·0°	1·85	83·0	3·9
Sodium	Na_2SO_4	142·0	13·4	15·0°	1·8	97·0	0·70
Magnesium	$MgSO_4$	120·4	36·2	20·0°	1·1	94·4	1·0
Zinc	$ZnSO_4$	161·4	50·9	15·0°	1·0	94·6	1·2
Aluminium	$Al_2(SO_4)_3$	342·3	36·1	20·0°	2·64	95·1	0·93
Ammonia alum	$Al_2(NH_4)_2(SO_4)_4$	474·4	6·25	15·0°	3·35	99·2	0·18
Sodium carbonate	Na_2CO_3	106·0	16·4	15·0°	2·0	94·6	1·3
Sodium bicarbonate	$NaHCO_3$	84·0	9·6	20·0°	(2·5)	95·0	0·95
Potassium carbonate	K_2CO_3	138·2	112·0	20·0°	3·4	57·3	8·2
Potassium bicarbonate	$KHCO_3$	100·1	33·2	20·0°	(3·0)	83·0	3·2
Potassium sulphocyanide	$KCNS$	97·2	217·0	20·0°	1·75	50·0	9·5
Potassium chromate	K_2CrO_4	194·2	63·2	20·0°	2·74	85·0	2·9
Potassium bichromate	$K_2Cr_2O_7$	294·2	12·0	20·0°	(3·0)	97·8	0·41
Ammonium bichromate	$(NH_4)_2Cr_2O_7$	252·1	9	15·0°	(3·0)	98·1	0·34
Potassium ferrocyanide	$K_4Fe(CN)_6$	368·3	32·0	20·0°	2·86	95·6	0·83
Potassium permanganate	$KMnO_4$	158·0	5·2	15·0°	(1·5)	99·1	0·20
Mercury fulminate	$HgC_2N_2O_2$	284·6	1·8	12·0°	(1·0)	99·9	0·03
Ammonium oxalate	$(NH_4)_2C_2O_4$	124·2	6·9	25·0°	(1·1)	98·9	0·18
Cane sugar	$C_{12}H_{22}O_{11}$	342·2	197·0	15·0°	1·1	90·0	2·3
Urea	$CO(NH_2)_2$	60·1	79·0	20·0°	1·0	81·0	3·6

American dynamites, containing as they do ungelatinized nitro-glycerine absorbed in a comparatively small quantity of wood-meal together with a deliquescent salt, are particularly liable to exude. The matter was investigated in 1908 by the "Bureau for the safe Transportation of Explosives,"[1] and three different tests have been adopted:

Pressure test.

(1) Pressure test. This is carried out in a glass tube 3 in. long and $1\frac{1}{8}$ in. internal diameter (sectional area 1 sq. in.). First 1·5 to 2 g. of cotton wool are placed in it, then 10 g. of the dynamite and then a second wad of 1·5 to 2 g. of cotton wool. The tube is placed upright on a vulcanite base, and a vulcanite disc is introduced into the tube above the upper wad, and on this a pressure of 80 lb. is exerted for one minute by means of a weight on a steel lever beam. The dynamite is then removed and weighed. The loss should not exceed 3 per cent. Dynamites which had absorbed much moisture were found to give up considerable amounts of nitro-glycerine in this test, as also did those with low proportions of wood pulp. A similar test is used in France. The explosive is placed in a bronze cylinder 15 mm. in diameter pierced with holes of 0·5 mm. In this it is subjected to a pressure of 5 kg. per sq. cm. (71 lbs. per sq. in.). The test is carried out at a temperature of 20° to 50° in comparison with a standard sample. A good gelatinized explosive shows no drops of nitroglycerine after an hour at 20° or after 20 minutes at 50°.[2]

Keeping test.

(2) Keeping test. A cartridge is kept in a vertical position for six days at a temperature of 40° C. The results of this test are generally in accordance with those given by the pressure test: if the latter shows an exudation of 5 per cent. or more, there is usually leakage at 40°. This, however, only applies to "straight" dynamites. If part of the wood-meal be replaced with kieselguhr, the explosive tends to give up much nitro-glycerine in the pressure test, but does not sweat badly at 40°. On the other hand, if a coarse material such as sawdust be used instead of wood-meal, very little nitro-glycerine is lost in the pressure test, but there is much exudation at 40° as also under service conditions.

Centrifugal test.

(3) The objection may be raised that the pressure of 80 lb. per sq. in. is very much greater than any that will occur in practice: in a packing case the pressure on the material is not likely to exceed 1 lb. per sq. in. A test was therefore devised, in which the dynamite is exposed to centrifugal force. The pressure upon any part of the explosive is very moderate in this case, but if there be a film of too great a thickness on each particle of absorbent, part of the liquid is removed by the centrifugal force. The machine used has brass cups measuring $1\frac{3}{8}$ in. × $5\frac{1}{8}$ in. inside, and the bottoms of the cups describe a circle of 7 in. radius. The machine is worked by hand by means of a crank 7 ft. long, and it is enclosed in a heavy wooden box to reduce the risk of the

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[1] *Bureau of Explosives Report*, Nos. 2 and 4; *S.S.*, 1910, p. 213.

[2] Vennin et Chesneau, p. 373.

operator. The sample is introduced into a glass tube exactly as in the case of the pressure test. It is then wrapped in cloth, and inserted into one of the cups, and the machine is rotated at 600 revolutions per minute for one minute. The loss should not be more than 3 per cent.

Sensitiveness or Danger in Handling

For general safety in dealing with explosives it is of great importance that they should not be too sensitive to blows or friction. A number of different tests have been devised for ascertaining the sensitiveness. A simple test consists of striking some of the explosive with a hammer; the severity may be varied not only by striking more or less violently, but also by placing the material on substances of different hardnesses. The explosive may be rubbed in a mortar, with or without the addition of sand or glass powder to increase the friction. Or it may be rubbed between pieces of wood covered with sand- or emery-paper. It may be shot at with a rifle; the severity of this test depends, of course, on the velocity of the bullet: it is also made more severe if the explosive be supported on a surface inclined to the direction of impact, or if the layer of explosive be of considerable thickness.[1] Ordinary gunpowder is not safe under the impact of bullets.[2] In all these and similar tests the explosive should always be compared with a standard explosive of a like nature. The standard explosives and tests adopted by the German Railway Commission will be found in Appendix I.

The following test was communicated by the late Dr. Dupré, Chemical Advisor to H.M. Inspectors of Explosives:[3] A small quantity of the explosive is spread on a large stone table and is struck a glancing blow with a mallet; the explosive is thus subjected to the combined effect of shock and friction. Use is made of two sorts of mallets, one of green hide and the other of beech wood. They are similar to those used by wood carvers. The hide mallet weighs about 12 ounces and the wooden one about 11½ ounces. The hide mallet is the more effective especially with chlorate explosives. If the sample explodes in this test it is repeated, using a broomstick instead of the mallets. The broomstick is held on the stone at an angle of about 60°, and a blow is struck with the end, taking care that the movement of the stick is in the direction of its axis. If an explosion is obtained in this way, the test is repeated, using a hard wooden table instead of the stone one, and finally if necessary a soft wooden table. If an explosive, other than those used for caps, detonators, etc., explodes even partially on soft wood, it is considered too sensitive to authorize its use. It need hardly be said that the mallets, broomstick and tables must be quite clean.

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[1] Hess, *Ang.* 1904, p. 546.

[2] Vennin et Chesneau, p. 122.

[3] *First Report of International Committee on the Stability of Explosives.* Brussels, 1908.

Friction test.

The U.S. Bureau of Mines has adopted an apparatus for testing the sensitiveness of explosives to friction, consisting of a steel anvil and a steel shoe, which swings at the end of a long arm and can be loaded with different weights. The anvil has a smooth face, and the shoe can be faced with fibre, steel, or other material. A few grammes of explosive are placed on the anvil, and the shoe is allowed to swing down from a known height and give it a glancing blow. The test is devised to represent what may happen in mining when a cartridge of explosive becomes lodged in a drill-hole and must be forced home by ramming.[1]

Falling weight test.

None of the above tests permit of the sensitiveness of the explosive being expressed by a definite figure, hence the advantage of the falling weight test, which allows the sensitiveness of quite different types of explosive to be compared. The evolution of the apparatus and method, in order to obtain constant and reliable results, was traced by Lenze at the 6th International Congress of Applied Chemistry,[2] and the matter was further dealt with by Kast at the 7th Congress in 1909. The following conditions must be fulfilled by the apparatus: The anvil must rest on a firm masonry foundation. The weight must not fall directly upon the explosive, but upon a bolt, C. (Fig. 81), which transmits the impact to the material under test, E, which rests on the anvil B. Both the bolt and anvil are made of hardened steel and can be ground down or renewed as soon as they become damaged. The sleeve, D, allows the stamp to move easily in a vertical direction, but permits no lateral

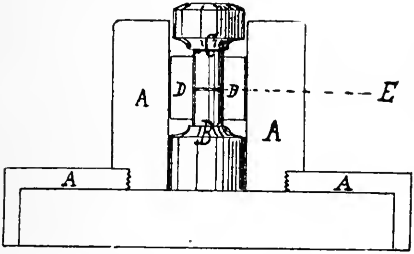

Fig. 81. Anvil, etc., of Falling Weight Apparatus

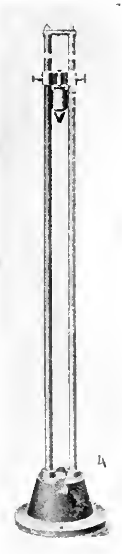

Fig. 82. Falling Weight Apparatus (E. A. Lenze, Berlin)

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[1] *Bureau of Mines Bulletin* 66, 1913, pp. 15, 290.

[2] *Report*, vol. 2, p. 522; *S.S.*, 1906, p. 287.

movement, so that the explosive is subjected to impact only, and not to friction. The whole is held in position by the base. A. Fig. 82 shows the whole apparatus. Lenze and Kast use anvils and bolts with an area of 0·5 sq. cm., but the apparatus of the American Bureau of Mines has a diameter of 1 cm. (area 0·785 sq. cm.), and at the 8th Congress it was resolved to adopt a diameter of 0·5 in. (1·27 cm., area 0·997 sq. cm.).[1] Weights of different sizes are used, but those of 2 and 10 kg. are the usual ones: the German Railway Commission tests all explosives with both of these. The results are influenced by the quantity of explosive used: in order to have a layer of the same thickness in every case it is better to measure the quantity rather than weigh it; the actual weight is generally 0·02 to 0·04 g., and the thickness of the layer about 1 mm. For the larger area adopted by the 8th International Congress the quantity of explosive is 0·05 to 0·1 g. If the quantity be increased it becomes less sensitive. In order to have the material in the state of maximum sensitiveness it should be dried for twenty-four hours over calcium chloride. It is usually wrapped in tin foil, and sometimes it is pressed into a flat tablet beforehand. The results are affected by the temperature at which the experiments are carried out: at 30° to 40° the length of fall is about 25 per cent. less than that required at 12° to 14°. The usual standard temperature is 18° to 20°; the anvil in some instruments is surrounded by a water jacket to facilitate the regulation of the temperature. The results are also affected by the physical condition of the explosive, the size of the grains, etc. A fresh quantity should be taken for each test, and the surfaces of the anvil and bolt carefully cleaned every time. This is specially important in the case of substances, such as picric acid, which form explosive compounds with iron.

The following classification of explosives according to their sensitiveness was given by Will at the 6th International Congress:[2]

		Length of fall cm.
Class I.	Cap decompositions and substances of similar sensitiveness, which detonate on ignition and are not allowed to be transported	0–7
	Mercury fulminate	2
	Nitro-glycerine, dry	4
	Lead picrate	5
	Silver picrate	5
	Iron picrate	7
	Copper picrate	7
	Dinitro-glycerine	7
Class II.	Dynamites. Very sensitive to blows, burn vigorously or deflagrate when ignited. Danger of explosion present	7–25
	Guhr dynamite, plastic	7

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[1] *See* end of this chapter.

[2] *S.S.*, 1906, p. 209.

		Length of fall cm.
	Blasting gelatine, plastic	12
	Blasting gelatine, frozen	12–15
	Gelatine dynamite, plastic	17
	Guhr dynamite, frozen	20
	Guhr dynamite from dinitro-glycerine, dry	25
	Blasting gelatine from dinitro-glycerine, dry	25
Class III.	About	26–100
	(*a*) Black powder. Not very sensitive to blows. Easily ignited. With safety fuse deflagrates. Danger of explosion not absent.	
	Sporting powder	70
	Blasting powder	85
	Black powder, coarse grain	100
	(*b*) Chlorate explosives. Moderately sensitive to blows, difficult to light, not ignited by safety fuse. Danger of explosion not absent.	
	Cheddite 60	32
	Cheddite 41	36
	(*c*) Aromatic nitro-compounds. Sensitive to blows. Difficult to light, not ignited by safety fuse. Danger of explosion not absent.	
	Tetranitro-methylaniline	40–65
	Hexanitro-diphenylamine	40
	Trinitro-benzene	40–50
	Trinitro-toluene	57–180
	Ammonium picrate	80
	Sodium picrate	80
	Trinitro-dimethylaniline	95
	Trinitro-cresol	30
	Picric acid	35–95
	(*d*) Nitro-cellulose with 15 per cent. water. Little sensitive to blows. Difficult to light. Not ignited by safety fuse. Danger of explosion not absent.	
	Gun-cotton, with 15 per cent. water	85
	Collodion cotton, with 15 per cent. water	100
	(*e*) Smokeless powders. Fairly sensitive to blows. Comparatively easy to light, burns rapidly or deflagrates when ignited with safety fuse. Danger of explosion almost absent.	
	Cube powder (nitro-glycerine)	20–30
	Sporting powder	30–45
	Rottweil flake powder	32
	Flake powders	30–54
Class IV.		100–200
	(*a*) Safety (in handling) explosives. Little sensitive to blows. Difficult to light, not ignited by safety fuse. Danger of explosion absent.	
	Roburite Ia	105
	Ammon-carbonite	110

	Length of fall cm.
Astralite	110
Donarite	110
Fulmenite. Wetter-fulmenite . . more than	180
Rottweil safety powder . ,,	180
Anagon-sprengpulver ,,	180

(*b*) Aromatic nitro-compounds with lower nitrogen-content than Class III (*c*). Little sensitive to blows. Difficult to light, not ignited by safety fuse. Danger of explosion absent.

Dinitro-benzene	120
Dinitro-phenol	150
Trinitro-xylene	170
Trinitro-naphthalene	175

(*c*) Nitro-cellulose with over 20 per cent. water. Insensitive to blows. Difficult to light, not ignited by safety fuse. Danger of explosion absent.

Gun-cotton, with 20 per cent. water . more than	185
Collodion cotton, with 20 per cent. . ,,	185

These results were obtained with a weight of 2 kg. falling on to a steel bolt resting on 0·1 g. of the substance, which was previously dried at 40°, except where otherwise stated. These results are in fairly good agreement with those obtained by others,[1] but for the more insensitive explosives it is better to increase the weight rather than have falls as long as 1·8 metres. The results with frozen blasting gelatine are not in agreement with those obtained in England with thicker layers.[2]

The following Table of the sensitiveness of various explosives when tested with different weights gives the results published by Bichel [3] and Brunswig [4]:

Explosive	Composition	Fall in cm. required to cause explosion						
		Falling weight in kilogrammes						
		0·1 kg.	0·25 kg.	0·5 kg.	1·0 kg.	2·0 kg.	5·0 kg.	20 kg.
Nitrogen iodide	NI_3	(*b*) 5						
Mercury fulminate	$HgC_2N_2O_2$	5–10	(*b*) 5					
Nitro-glycerine	$C_3H_5(NO_3)_3$	5–10	(*b*) 5					
Guhr dynamite .	75 N G 25 Guhr	5–10	(*b*) 5					

(*b*) means below.

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[1] *See* Bichel, *Marine-Rundschau*, 1905, p. 1345; *S.S.*, 1906, p. 14; Zschokke, ***Militarische** Sprengtechnik*, 1911.

[2] *See* Chap. xvii.

[3] *Marine-Rundschau*, 1905, p. 1345.

[4] *Explosivstoffe*, 1907.

Explosive	Composition	Fall in cm. required to cause explosion						
		Falling weight in kilogrammes						
		0·1 kg.	0·25 kg.	0·5 kg.	1·0 kg.	2·0 kg.	5·0 kg.	20 kg.
Gelatine dynamite	63·5 N/G 1·5 N/C 27·0 $NaNO_3$ 8·0 Wood-meal	5–10	(*b*) 5					
Dinitro-glycerine	$C_3H_5(NO_3)_2OH$	10–15	5–10	(*b*) 5				
Gel. dyn. made from it	63·5 D/n/G 1·5 N/C 27·0 $NaNO_3$ 8·0 Wood-meal	30–35	15–20	5–10	(*b*) 5			
Pot. Chlorate and sulphur	$KClO_3 + S$	15–20	10–15	5–10	(*b*) 5			
Gun-cotton, dry		30–40	15–20	5–10	5–10	5–10	(*b*) 5	
Flake powder .	Gelatinized N/C	40–50	20–30	10–15	10–15	10–15	5–10	(*b*) 5
Gun-cotton, wet	15 per cent. H_2O	(*a*)200	70–80	15–20	10–15	10–15	5–10	(*b*) 5
Black powder .	75·0 KNO_3 10·0 S. 15 0 Charcoal		(*a*)200	190–200	100–110	30–40	5–10	(*b*) 5
Picric acid, crystalline	$C_6H_2(NO_2)_3OH$			(*a*) 200	190–200	100–110	50–60	(*b*) 5
Picric acid, compressed	$C_6H_2(NO_2)_3OH$				(*a*) 200	140–150	80–90	(*b*) 5
Trinitro-toluene, crystalline	$C_6H_2(NO_2)_3CH_3$			(*a*) 200	180–190	90–100	50–50	(*b*) 5
Trinitro-toluene, compressed	$C_6H_2(NO_2)_3CH_3$				(*a*) 200	150–160	80–90	(*b*) 5
Gelatine-carbonite	25·3 N/G 0·7 N/C 41·5 NH_4NO_3 6·9 Glyc. jel. 25·6 NaCl	80–90	20–30	5–10	5–10	5–10	(*b*) 5	
Kohlen-carbonite	25 0 N/G 34·0 KNO_3 1·0 $Ba(NO_3)_2$ 38·5 Flour 1·0 Tan 0·5 Soda	(*a*)200	50–60	20–30	20–30	20–30	5–10	(*b*) 5

(*a*) means above, (*b*) below.

Explosive	Composition	Fall in cm. required to cause explosion						
		Falling weight in kilogrammes						
		0·1 kg.	0·25 kg.	0·5 kg.	1·0 kg.	2·0 kg.	5·0 kg.	20 kg.
Carbonite	30·0 N G 24·5 $NaNO_3$ 40·5 Flour 5·0 $K_2Cr_2O_7$	60–70	30–40	10–20	10–20	10–20	(*b*) 5	
Ammon-carbonite	4·0 B G 82·0 NH_4NO_3 10·0 KNO_3 4·0 Flour	(*a*)200	(*a*)200	170–180	100–110	40–50	15–20	(*b*) 5
Donarite	3·8 N G 0·2 N C 80·0 NH_4NO_3 12·0 T n T 4·0 Flour			(*a*) 200	120–130	60–70	15–20	(*b*) 5
Grisounite couche	95·5 NH_4NO_3 4·5 T n n				(*a*) 200	140–150	70–80	(*b*) 5
Roburite II	71·5 NH_4NO_3 5·0 KNO_3 6·0 Flour 0·5 $KMnO_4$ 5·0 NaCl 12·0 T n T				(*a*) 200	70– 0	50–60	(*b*) 5

(*a*) means above, (*b*) below.

The determinations were carried out with quantities of 0·1 g. wrapped in tin-foil.

The U.S. Bureau of Mines has recently adopted a much larger apparatus in which a weight of 200 kg. is used and can be dropped as much as 7·5 metres. In this apparatus 20 g. of explosive are used each time. It is claimed that with this larger charge the results are more reliable and represent more closely the relative sensitiveness of explosives to direct impact. They are not parallel to those obtained with a smaller apparatus.[1]

The sensitiveness of an explosive is increased by making it more compact and rigid so as to localize the effects and transform them into heat, also by mixing it with a hard angular substance so as to increase the friction and the local shocks. On the other hand the sensitiveness is decreased by pulverizing it very finely so as to increase the mobility of the particles, or by mixing it with a soft plastic substance.[2]

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[1] *Bureau of Mines Bulletin* 66, 1913, pp. 17, 287.

[2] Vennin et Chesneau, p. 121.

Sensitiveness to detonation

Sensitiveness to detonation is ascertained by firing cartridges with detonators of varying strength to discover the weakest that will detonate it completely. The action of fulminate of mercury and similar substances resembles that of a blow rather than of a flame, so the results of this test are on the whole parallel with those obtained by the falling weight test. Explosives for use in coal-mines when tested for safety are fired into the testing galleries without any stemming, so that it is necessary that they should detonate completely when fired with a No. 7 or 8 detonator unconfined. Explosives for military purposes also must detonate unconfined, but those usually used, trinitro-toluene, picric acid, wet gun-cotton, require special detonators or a priming of some powerful explosive.

The detonators used for this test must, of course, be reliable and uniform in strength. The density of the explosive greatly influences its sensitiveness to detonation: the denser it is, the more difficult it becomes to detonate it. At a high density many ammonium nitrate and chlorate explosives become practically inexplosive; even if detonation be started by means of a powerful priming, it is not propagated throughout the mass, but dies away leaving part of the explosive unconsumed. Substances are generally less difficult to detonate when reduced to powder than when in large crystals, but the powder is less sensitive to blows. From a blow the fine material apparently escapes without being subjected to much shock, but the effect of the detonator is concentrated on a smaller mass of material.[1] If unconfined a finely powdered explosive may be scattered without being detonated completely, but if confined it is more easily detonated than the coarse crystalline material. Frozen nitro-glycerine explosives are much less sensitive to detonation, whereas to blows under some conditions they are more sensitive.

From experiments with fulminates and various other initiators L. Wöhler places explosives in the following order of diminishing sensitiveness to detonation: [2]

Tetryl
Picric acid
Trinitro-cresol
Trinitro-resorcinaol
Trinitro-benzoic acid
Trinitro-toluene
Trinitro-anisole
Trinitro-xylene

Dry guncotton is somewhat more sensitive than picric acid, and trinitrobenzene slightly more so than trinitro-toluene,[3] tetranitro-aniline about the same as tetryl.

Taylor and Cope have found that the addition of a small proportion of

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[1] *See* Hess, *Ang.*, 1904, p. 546.

[2] *Ang.*, 1914, 1, p. 335; *S.S.*, 1914, p. 242.

[3] *S.S.*, 1907, p. 268.

tetryl to trinito-toluene renders the mixture almost as sensitive as pure tetryl.[1]

Sensitiveness to detonation can also be measured by ascertaining the proportion of oil that can be added without rendering the explosive inert, as in Esop's test.

Effect of temperature.

At high temperatures explosives are considerably more sensitive: conversely their sensitiveness is reduced by cooling them. The following Table shows the quantity of fulminate in grammes required to detonate various explosives when cooled to about −80° by means of solid carbon dioxide and acetone, or to about −190° with liquid nitrogen.[2]

Explosive	Density	Grammes fulminate required		
		Ordinary temperature	−80°	−190°
Fulminate	1·20	<0·25	—	1·0
Blasting gelatine	—	<0·25	0·25	1·0
Cheddite No. 2	1·00	0·25	0·75	>2·0
Picric acid	0·90	0·25	1·0	>2·0
Gun-cotton	0·40	0·25	0·25	>2·0

In these experiments the detonator was cooled as well as the explosive, and the effect is partly due to reduced efficiency of the detonators at low temperatures. It was found that if the detonator was cooled to −190°, it was necessary for it to contain 1 g. of fulminate in order to detonate uncooled picric acid (density 1·0), whereas with the detonator at the ordinary temperature 0·25 g. sufficed.

Transmission of detonation.

An allied property is that of transmitting detonation from one cartridge to another across an intervening space by "influence." The more sensitive an explosive is, the greater is the distance at which it can be exploded, but the distance is also affected by the violence of the impulse given by the first cartridge, which again depends to a considerable extent upon the velocity of detonation. Another factor is the nature of the surface on which the cartridges are resting. They are often placed on a steel rail: on soft ground the distance is less, and if they are suspended in the air less still. The last arrangement offers the advantage of a fairly constant universal medium, but the objection may be raised that the conditions are fundamentally different from those prevailing in practice: the relative values for explosives of similar type probably remain much the same, however. If the two cartridges are placed in a roll of paper, the detonation is transmitted over a

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[1] *U.S. Bureau of Mines Technical Paper*, No. 145.

[2] A. Kling and D. Florentin. *P. et S.*, vol. xvii., 1913, p. 145.

greater distance than if they are quite unconfined. A simple method of determining the distance of transmission is to set out a row of small cartridges at increasing distances and ascertain how many of them explode when the end cartridge is detonated. The results depend on the density of the explosive among other factors; for on the one hand an increase in density increases the velocity of detonation, but on the other it makes the explosive less sensitive. With cartridges of greater diameter the transmission is naturally better. These tests are carried out with the cartridges arranged end on to one another. It is important that the transmission shall not be too poor, because this involves danger that, if for any reason the different cartridges are separated from one another by moderate intervals, the whole of the charge will not be detonated. Some explosives transmit so badly when frozen that detonation is incomplete even when there is no break in the continuity of the charge.

Total or partial failure to detonate is a frequent cause of accidents, as the explosive is liable to go off during subsequent handling of the material that is being blasted. Accidents also occur in drilling fresh holes near unexploded charges. The "P.P. apparatus" has been devised to obviate this danger by safely withdrawing the detonator and replacing it.[1]

Some interesting experiments were made by Comey on the velocity with which detonation is transmitted from one cartridge of explosive to another.[2] The explosives used were American "straight dynamites" of various strengths. Half sticks were wrapped in paper leaving one end exposed, and these were laid on the ground with the exposed ends facing one another. Into these ends were inserted detonators, which were connected together by detonating fuse, so that the time of transmission could be measured by Dautriche's method. The following results were obtained.

Strength of Dynamite	Normal Velocity of Detonation	Velocity of Transmission of the Wave of Detonation through the Air Metres per second								Limit of Sensitiveness
		5″ (127 mm.)	10″ (254 mm.)	15″ (381 mm.)	20″ (508 mm.)	25″ (635 mm.)	28″ (711 mm.)	30″ (762 mm.)	40″ (1016 mm.)	
Per cent.										
60	5795	5346	5224		4295		—	3852	2733	48″ (1219 mm.)
40	4796	4500	4196	—	3537	—	—	2714	2253	40″ (1016 mm.)
30	4311	—	3489	—	3159	—	—	—	—	42″ (1067 mm.)
25	3349	3426	3502	3250	2939	2572	2357	—	—	28″ (711 mm.)
20	3297	—	3103	—	2665	—	—	—	—	32″ (813 mm.)
60	—	—	5260	—	4372	—	—	3567	whole	sticks
40	—	—	4610	—	3791	—	—	2908	,,	,,

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[1] *See A.R.* 1913, pp. 42, 43.

[2] *Report of 7th Int. Cong. Appl. Chem.*, vol. iiib., p. 30.

If these results are recalculated so as to give the velocities over each interval instead of the mean velocity from the start, the following are the figures :

Strength of Dynamite	Normal Velocity of Detonation	0–10″	10–20″	20–30″	30–40″
Per cent.					
60	5795	5183	3650	3175	1460
40	4796	4215	3110	1710	1490
30	4311	3489	2880	—	—
25	3349	3503	2560	1733 [1]	—
20	3297	3103	2340	—	—
60	5795	5260	4390	2620	—
40	4796	4610	3220	1990	—

[1] 20–28″.

Considering that each result was obtained with a different cartridge the figures are fairly regular. The wave set up in the air apparently starts with about the same velocity as that of the detonation of the explosive, and then the velocity decreases at the rate of about 50 metres per second for every cm. traversed.

The "limits of sensitiveness" given by Comey are high, and were no doubt affected by the presence of a detonator in the end of the second cartridge ; they represent in fact the distances at which a detonator is fired by the explosives. The standard dynamite of the Pittsburgh Testing Station, which has the composition :

Nitro-glycerine	40
Sodium nitrate	44
Wood pulp	15
Calcium carbonate	1

transmits to another cartridge with no detonator only over a distance of 17 inches, both cartridges being suspended in the air. Carbonites, which contain less nitrate and more wood-meal and other constituents transmit only to distances of 2 inches to 9 inches. An explosive consisting of ammonium nitrate with 6·6 per cent. trinitro-toluene and 4·2 per cent. nitro-naphthalene would not transmit with certainty even to ½-inch, but another ammonium nitrate explosive containing nitroglycerine transmitted to 2 inches.[1] All these results were obtained with cartridges 1¼ inches in diameter and 8 inches long suspended in air end to end.

The distance to which transmission takes place depends upon the size of the first charge ; C. E. Bichel[2] gives the following figures for gelatine dynamite :

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[1] *U.S. Bureau of Mines Bulletin* No. 15.

[2] *Testing Explosives*, p. 49 and Table I.

1	kilogramme	0·80 metres
5	,,	1·45 ,,
10	,,	1·80 ,,
25	,,	2·25 ,,
50	,,	2·50 ,,
100	,,	2·75 ,,
200	,,	5·25 ,,

At an accidental explosion of nearly 9½ tons of dynamite and blasting gelatine at Keeken two lots of dynamite each of 150 kg. at distances of 40 and 50 metres respectively were exploded by transmission, but a third lot 70 metres away remained intact. When the explosives are placed underground, explosion is transmitted to much smaller distances than when they are above ground. From these facts Bichel concluded that the transmission was by the flame rather than by shock. But as many explosives only burn when ignited by a flame, this explanation is not satisfactory. Moreover it is not in agreement with Bichel's own figures reproduced in the following table:

Explosive	Length of Flame from 100 g.	Distance of Transmission
Dynamite, No. 1	228 mm.	310 mm.
Gelignite	150 mm.	250 mm.
Donarite	69 mm.	60 mm.
Ammon-Carbonite I	56 mm.	60 mm.
Ammon-Carbonite	51 mm.	50 mm.
Thunderite	43 mm.	30 mm.
Carbonite II	48 mm.	190 mm.
Carbonite I	45 mm.	190 mm.
Kohlen-Carbonite	41 mm.	150 mm.
Carbonite	40 mm.	200 mm.

The tests were carried out with cartridges of 1¼ inch diameter laid on the ground, the weight and length of the cartridges are not stated. The explosives containing nitroglycerine all transmitted explosion to distances considerably over 100 mm. and those not containing it to distances considerably less than 100 mm. The bad transmission through earth is probably due to the discontinuity of the medium and the work done on the earth itself. The following results have been obtained in France:[1]

Explosive	Distance of transmission
Petard of dry compressed gun-cotton, 100 g.	800 mm. about
Dynamite	1000–1800 according to conditions
Cheddites	30–40

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[1] Vennin et Chesneau, p. 118.

Sensitiveness to heat.

The danger in the handling and transport of an explosive depends very largely on its behaviour when exposed accidentally to heat, flame or spark. Will's classification on pp. 424 to 426 is based very largely on this. An explosive which catches fire easily, or explodes when it comes in contact with fire, is much more dangerous than one that can only be lit with difficulty and then burns quietly. As in the case of sensitiveness to blows and friction these properties are of even more importance in explosives intended for military use than in ordinary mining explosives. Kast [1] gives the following tests:

Behaviour at Temperatures near the Ignition Point. The ignition point is ascertained by the method given in Appendix I. Then in a second experiment the bath is heated to this temperature with the empty test-tubes in it, and the explosive is only then introduced into them. In a third experiment the bath is heated to a temperature 10° above the ignition point, and in a fourth 10° (or 20°) below it. Every test is repeated two or three times. The time until the material puffs off is taken as the measure of its sensitiveness. Of black powder, ammonium nitrate and chlorate explosives 0·5 g. is taken each time: of dynamites or nitro-celluloses 0·1 g.

Behaviour towards Direct Ignition. A small quantity (5 to 10 g.) is ignited on an iron plate with a burning splinter of wood, a second with a red-hot iron wire, and a third by throwing it into a red-hot iron basin, and it is observed whether it burns slowly, or fast, or puffs off. The test is made more severe if the explosive be heated beforehand to a high temperature (100° to 200°), and is then ignited.

A portion of 3 g. of the explosive is placed loosely in a short test tube, and a piece of safety fuse is inserted into the middle of it. It is observed whether the material deflagrates, when the fuse burns down to it.

Finally a considerable quantity of the explosive packed in a box is introduced into a fierce fire.

It is thus ascertained whether the explosive is liable to explode. Black powder and similar explosives behave the worst under these circumstances: then follow dynamite, chlorate explosives, then the nitro-compounds such as picric acid, and finally the practically incombustible ammonium nitrate explosives.

The tests adopted by the German Railway Commission are given in Appendix I. The Table on p. 435 gives the results of the standard explosives:

Temperature of ignition.

In order to determine the temperature of ignition a small sample of the explosive, usually 0·1 g., is placed in a small test-tube, which is then tightly corked and placed in a paraffin bath at 100°. The bath is now stirred and heated so that the temperature increases 5° per minute. The temperature is noted at which the sample explodes. The following are the lower limits

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[1] *Spreng- und Zündstoffe*, p. 1017.

Standard explosive	Safety fuse test	Red-hot iron basin	Ignition point in metal bath	In iron box in fire
Donarite	No ignition	No explosion	(*a*) 250°	No explosion
Picric acid	,,	,,	300°	Burns rapidly. No explosion
Tetranitro-methylaniline	,,	,,	190°	Burns with occasional puffs
Cheddite	,,	,,	(*a*) 200°	Slight deflagration
Silesia	,,	,,	(*a*) 200°	Vigorous deflagration
Blasting saltpetre	Burns. No detonation	Burns rapidly. No detonation	300°	
Black powder (sporting)	,, ,,	Puffs off at once. No explosion	300°	
Guhr dynamite	Ignites. No explosion	Burns without explosion	207°–215°	
Blasting gelatine	,, ,,	,, ,,	207°–211°	

(*a*) means above.

of the explosion temperatures for satisfactory samples, as required by the United States Ordnance Department : [1]

Nitro-cellulose	186°
Nitro-cellulose powder	177°
Nitro-glycerine ,,	170°

The results are found to be reliable when the explosive is either very good or very bad.

Fig. 83 shows an apparatus that is used in Spain for determining the temperature of ignition. The copper bar, *a*, has a circular enlargement at one end, in which there are five holes ; the central one, *F*, contains mercury, in which the bulb of a thermometer is immersed ; in each of the others is placed a copper tube containing 0·1 g. of the explosive to be tested. The bar is supported on a stand, and is heated by means of burners placed underneath it : the rate of heating can be regulated by moving the burners. The explosive in tube *b* explodes first, then *c* and *d*, and finally *e*. The mean of the readings of the thermometer when the explosions occur is taken as the temperature of ignition. If this temperature be above 180° the explosive (presumably nitro-cellulose powder) is considered good ; if between 178° to 180° it is

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[1] *See* A. P. Sy, *J. Frank. Inst.*, 155, 1903, p. 161 ; *J. Amer. Chem. Soc.*, 1903, p. 549.

serviceable; if between 176° and 178° it is sentenced to immediate expenditure; if below 176° to destruction.[1]

The method adopted by the German Railway Commission for determining the temperature of ignition is given in Appendix I, as also a method for ascertaining the time required for igniting a small quantity at a temperature of 145°. Finzi has given the results of a considerable number of determinations of the temperature of ignition of nitro-cellulose in various states of stability, and also of smokeless powders.[2]

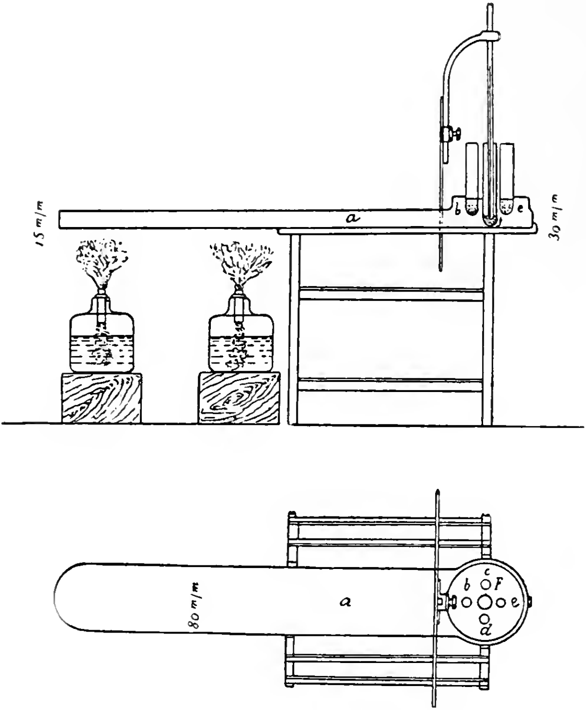

FIG. 83. Apparatus for Determining the Temperature of Ignition

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[1] *First Report of Intern. Commission, Brussels*, 1908, p. 60.

[2] *Gazzetta Chimica Italiana*, 1909, p. 549; *S.S.*, 1910, p. 153.

Dupré found that determinations of the temperature of ignition gave fairly concordant results, but that they were influenced by many conditions, such as the temperature at start, the rate of rise of temperature, the size of the tube, and the weight of explosive. Samples of very different stability do not give very different results.[1]

Time of ignition.

In order to measure the time required to ignite an explosive A. W. Cronquist fastens a small portion on the end of a pendulum which swings through a flame under such conditions that it is possible to estimate the time.[2] A somewhat similar apparatus had been described by N. C. Hansen.[3]

International Committee.

The International Committee on Tests for Explosives has adopted the following methods for the examination of commercial blasting explosives, to ascertain whether they are safe enough for transport.[4]

I. *Preliminary Test.* Two portions, each of 10 g. of the explosive not dried, are placed in glass capsules loosely covered, 25 mm. in diameter and 50 mm. high. They are placed in an oven heated to 75°, where they remain for forty-eight hours. No decomposition must have occurred in the explosive, nor must there be any notable change in its appearance or smell. In the case of nitro-explosives there must be no formation of red fumes.

II. *Falling Weight Test.* Equal weights of the explosive under examination previously powdered and dried, on the one hand, and of pure picric acid powdered and dry, on the other, are tested in the same apparatus under identical conditions. The portions taken, 0·05 to 0·1 g. each, are placed on a steel anvil in the form of a layer 1·27 cm. ($\frac{1}{2}$-inch) in dimater. On top of the explosive is placed a cylinder of tempered steel, 1·27 cm. in diameter and the same in height. Ten consecutive tests are carried out with each of the explosives in order to determine the mean height of fall necessary to cause explosion.

To be considered insensitive to shock, the explosives must not be more sensitive than pure powdered picric acid.

II*b*. *Friction Test.* The explosive, placed in an unglazed porcelain mortar gently warmed (20° to 30°), must not prove more sensitive than pure powdered picric acid submitted in the same apparatus to identically the same test.

III. *Sensitiveness to Ignition.*

(*a*) Fuse Test. Three g. of the powdered explosive are placed in a glass test-tube. By gentle tapping the substance is given an even surface. Then a slow-burning fuse (1 cm. per second) is intro-

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[1] *A.R.*, 1904, p. 28. [2] *S.S.*, 1906, p. 106. [3] *S.S.*, 1913, p. 165.

[4] *Report of 8th Inter. Cong. Appl. Chem.*, vol. 25, p. 261. The Committee published an English version of the Instructions, but I have preferred to make a translation of the original French.

duced. The test is repeated twice. If ignition occurs, the substance is classified as a deflagrating powder or a readily inflammable explosive.

(*b*) Red-Hot Iron Basin Test. If the explosive has passed the last test without igniting, it is submitted in this test to a high temperature to make sure that it is not liable to explode when exposed to fire.

A hemispherical iron basin 12 cm. in diameter and 1 mm. thick is heated red hot on a burner; a small quantity (0·5 g.) of the powdered substance is first introduced, then if there be no explosion the quantity is increased up to 5 g. The test is carried out three times.[1]

(*c*) The Red-Hot Iron Test is to ascertain the inability of safety explosives to burn. After some preliminary trials with small quantities to ascertain that the product has comparatively little tendency to burn, 100 g. of the explosive are placed on an asbestos card; the end of an iron bar 15 mm. in diameter, heated to a cherry red (about 900°) for a length of 10 cm., is then brought into contact with the explosive. The substance must only burn slowly, without exploding at all, and the flame must die out when the source of heat is withdrawn.

The effect of these three groups of tests is to divide explosives into three classes:

(1) Explosives sensitive to mechanical action will give results inferior to picric acid in tests II and II*b*; this class includes dynamites and certain chlorate explosives.

(2) Gunpowder and similar explosives will fail in test III*a*.

(3) Ammonium nitrate explosives will generally pass tests III*b* and *c*, as also will other explosives that possess a high degree of safety in transit.

If an explosive after passing tests II, II*b* and III*a* explode in the red-hot basin (III*b*), it will be necessary to reduce it to class 1. But this is only likely to occur with certain types which are but little used.

An explosive which having passed tests II, II*b*, III*a* and III*b*, is found to burn with violence in test III*c*, would have to be classed with gunpowder (class 1), or be placed in a sub-class between the second and third classes.

British Classification.

In the British Empire explosives are classified according to the substances they contain and the form in which they are made up. The following are the main classes:

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[1] Tests III*a* and *b* are the same as those of the German Railway Commission given in Appendix I, tests A15(*a*) and (*b*).

Class 1. Gunpowder.
,, 2. Nitrate mixture.
,, 3. Nitro-compound.
,, 4. Chlorate mixture.
,, 5. Fulminate.
,, 6. Ammunition.
,, 7. Firework.

Class 1 comprises ordinary gunpowder, but has recently been extended to include that made with sodium nitrate. Class 3 comprises nitro glycerine and nitro-cotton as well as the substances that chemists call nitro compounds, also all mixtures containing these substances. In division 1 of this class are the explosives containing nitro-glycerine or other liquid "nitro-compound," in division 2 those not containing it. Class 2 comprises explosives containing a mineral nitrate, such as saltpetre or ammonium nitrate and not falling within class 1 or 3. Class 4 does not include perchlorate explosives; these are in class 2. Class 5 includes all substances which are highly sensitive, such as lead azide and mixtures of chlorate and phosphorus. Class 6 includes amongst other articles cartridges for blasting and for cannon. Full details of the classification are given in the Guide to the Explosives Act and in Annual Reports of H.M. Inspectors of Explosives.

CHAPTER XXIX

THE PRESSURE AND HEAT OF EXPLOSION

Heat of explosion : Calorimeters : Corrections : Means of igntion : Volume of gas : Pressure : Rodman's gauge : Crusher gauge : Rifle pressures : Shot-gun pressures : Recording pressure gauges : Relation of pressure to gravimetric density : Calculation of temperature from heat of explosion ; Specific heats of gases : Of solids : Products of explosion : Formation of methane : Of ammonia : Carbonates : Carbon : Aluminium : Calculation of temperature from pressure : Direct measurement of temperature : Examples of calculations.

Heat of Explosion

WHEN an explosive is fired, heat is always liberated, and the amount of this heat per unit weight of explosive is one of the most important factors governing the power of the explosive. Many explosives liberate practically the same amount of heat when exploded under very different conditions, others show slight variations, which, however, can be explained.

Calorimeters.

Calorimeter bombs for measuring directly the heat of explosion differ from those used for ordinary thermo-chemical work in that they have to be much stronger in order to withstand the high pressures generated. Berthelot in his early experiments used a light bomb in which he could only deal with a small quantity of explosive. Sarrau's "éprouvette calorimétrique," although it had a capacity of 300 c.c. could only take a charge of 3 g., because the walls were not very thick.[1] Noble and Abel in their classical *Researches on Explosives* were the first to use a very strong bomb (Fig. 84), in which as much as 500 g. of gunpowder could be exploded at a density exceeding 1.[2] The plug, C, carries an arrangement for firing the powder by means of a wire heated to incandescence by electricity ; K carries a crusher gauge for measuring the pressure generated, and E enables the gaseous products of explosion to be collected, measured and analysed. Afterwards the same investigators used the calorimeter shown in Fig. 85. Two bombs were used with this : one had a capacity of 32·5 c.c. and took 10 to 13 g. of gunpowder, the other had a capacity of 118·8 c.c. and took 26 g.[3]

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[1] *P. et S.*, vol. vii. p. 158.

[2] *Phil. Trans.* 1875.

[3] *Phil. Trans.* 1879.

Many modern explosives, especially those containing ammonium nitrate, can be exploded only by means of a detonator containing a fairly powerful charge of fulminate of mercury or similar substance. In order that the heat due to the detonator may be small in comparison with that of the explosive, it is desirable to fire a large charge. Bichel and Mettegang, not wishing to make their bomb too thick and heavy, enlarged its capacity to 30,000 c.c. It is bottle shaped, and has walls about 13 mm. thick, and weighs about 70 kg. This is placed in the cylindrical copper vessel shown in Fig. 86 containing a known volume of water, which is kept stirred mechanically; the copper vessel is placed inside the wooden tub to insulate it and protect it from draughts. Into the water dips a thermometer, which can be read to 0·001°: there is an arrangement for knocking this continually to prevent the mercury column sticking. The charge of explosive is suspended in the middle of the bomb. It is of course necessary to observe the precautions usual in calorimetric work. The calorimeter takes a charge of 100 g. of high explosive, or double the quantity of black powder.

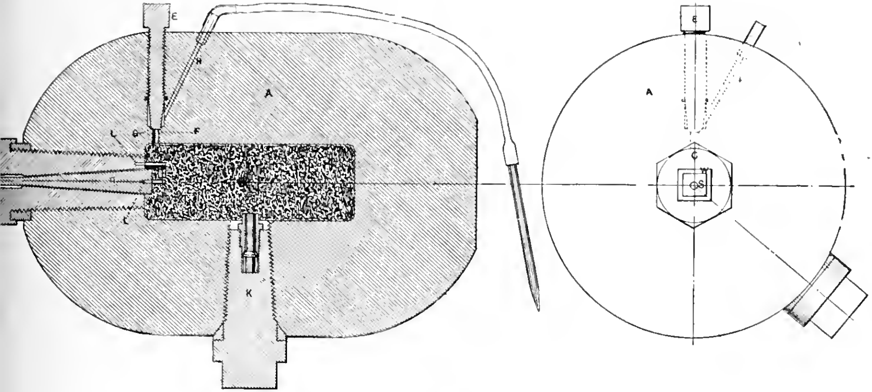

FIG. 84. Noble and Abel's Bomb

For studying the explosion of high explosives at high densities of charging there is at the Centralstelle, Neubabelsberg, a strong bomb of nickel steel with a capacity of about 45 c.c., which can take a charge of 20 g. All such bombs require to be very carefully designed and made, for if there be the least leak, the escaping gas at the high temperature and pressure will wash away the metal and perhaps make the bomb quite unserviceable. On the other hand, the closing plugs must not jam so tightly that the bomb cannot be opened.

Corrections.

The rise of temperature multiplied by the sum of the quantity of water in the calorimeter and the water equivalent of the apparatus and of the contents of the bomb, is the amount of heat produced by the explosion of the charge. But certain corrections have to be applied to obtain the true value. Under the experimental conditions the water produced is practically all condensed to liquid in the bomb, but when an explosive is actually used all the water is generated in the state of vapour, consequently the latent heat of condensation of the water must be subtracted from the heat found. Again, if there be any solid bases formed in the reaction, they will be converted by the carbonic acid present into carbonates or bicarbonates, and the heat liberated in this change must also be subtracted, as also the heat of solution of any soluble solids.

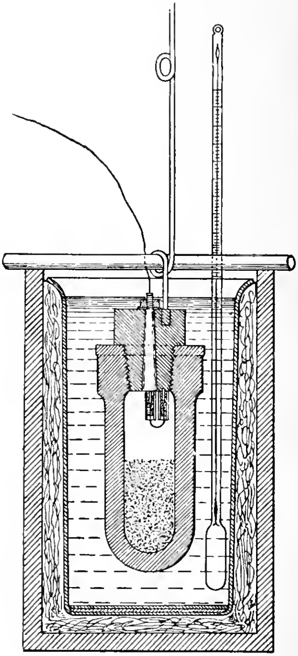

Fig. 85. Noble and Abel's Calorimeter

The condensation of 1 mol. of water liberates 10·9 large calories according to Berthelot, or 10·4 at a temperature of 18° according to Thomsen. The formation of the bicarbonates is shown by the equations :

$$Na_2CO_3 + CO_2 + H_2O = 2NaHCO_3 + 31{\cdot}0 \text{ Cals.}$$
$$K_2CO_3 + CO_2 + H_2O = 2KHCO_3 + 35{\cdot}4 \text{ Cals.}$$

the water being in the form of gas.

Means of ignition.

Allowance must also be made for the heat produced by the means of ignition. Unfortunately this depends not only on the nature of the igniter, but also in many cases on the composition of the gases given off by the explosion of the substance under investigation. If these gases contain an excess of oxygen, the heat due to a detonator, for instance, is much higher than if it be detonated by itself, or used for an explosive that produces a reducing atmosphere. Thus it was found at the Schlebusch works[1] that a No. 3 detonator (containing 0·255 g. fulminate and 0·045 g. potassium chlorate) gave 0·166 Cal. in a reducing atmosphere and 0·791 in an oxidizing one. The increase is due not only to the conversion of the carbon monoxide into dioxide, but also to the oxidation of the copper of the detonator and the insulating material of the

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[1] *S.S.*, 1907, pp. 281, 306.

wires. Hall gives the heat produced by a No. 7 detonator (1·5 g. charge) as 0·86 Cal. evidently fired in the absence of free oxygen ;[1] Biehel for a No. 8 detonator (2 g.) found 1·381 Cals.

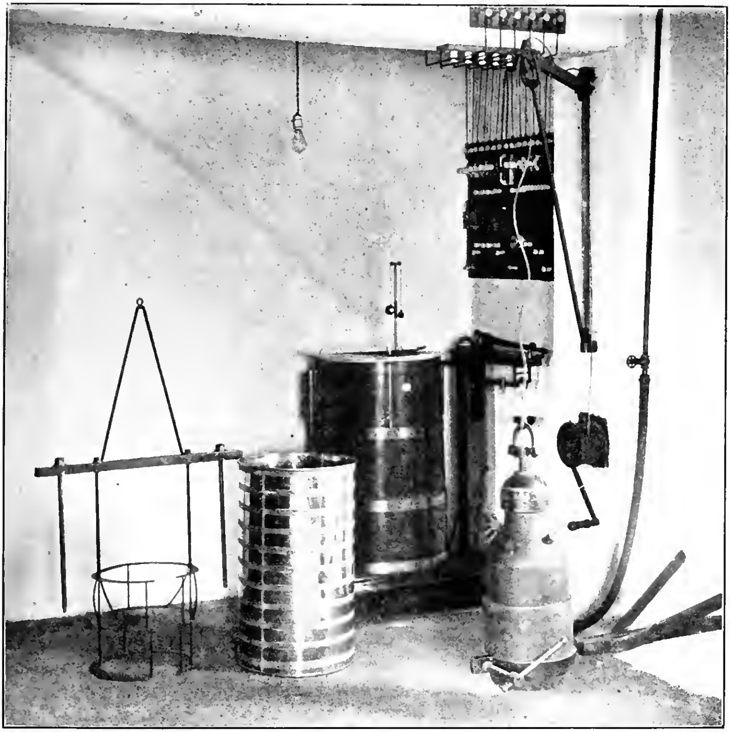

FIG. 86. Bichel and Mettegang's Calorimeter with Accessories

Volume of gas

The volume of the gases formed can be estimated in various ways. If the explosion has been carried out in a capacious vessel, so that the density is only about 0·01, it can be deduced from the pressure after the vessel and the products have cooled to the ordinary temperature ; but if this remaining pressure

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[1] *Bureau of Mines Bulletin* 15, p. 111.

be too high, the estimation is somewhat uncertain. It can also be calculated from their weight, as determined by weighing the vessel before and after allowing the gases to escape; if the density of the gases at atmospheric pressure be determined either by actual weighing or by calculation from the composition, the volume can then be deduced. Or again the whole of the gas can be collected and measured. As the volumes are large, special appliances are required for this: their design depends upon the magnitude of the charges to be dealt with.

The gases are analysed by the ordinary methods. The water can be driven out of the bomb by heating it in a bath of hot water and drawing a current of dry air through. The greater part of the water can be collected in a cold glass bulb and weighed, and the remainder can be absorbed in tubes filled with calcium chloride or sulphuric acid. It may be necessary to add to the volume of carbon dioxide found, that absorbed by the bases formed by the explosion, as noticed above. The gases usually formed as CO_2, CO, H_2, N_2, O_2, CH_4, and sometimes other hydro carbons, especially if the explosive contain metallic aluminium. Ammonia and oxides of nitrogen are also produced sometimes in small quantities, but are not generally estimated, partly on account of the difficulty of determining them without loss.

If the products of explosion be known, the heat liberated can be calculated from their known heats of formation and those of the original constituents of the explosive. The sum of the former minus the sum of the latter is the heat of explosion. In Appendix II are given the heats of formation of the principal materials that occur in explosives, as well as other data that are required for these calculations. The calculations made in this way agree well with the results obtained in the bomb calorimeter.

Pressure

The occasional bursting of fire-arms must have called attention early to the great pressure that is generated when gunpowder is fired in a confined space, but it was long before this pressure could be measured with anything approaching accuracy. In the eighteenth century Count Rumford attempted to measure it by exploding the powder in a small vessel with an orifice closed by a ball, and ascertaining the weight which sufficed to prevent the ball being lifted, but he obtained results which were many times higher than they should have been.

Rodman's gauge.

The first instrument that gave results approaching accuracy was the gauge invented in 1861 by Major Rodman of the United States army. A hole was bored in the wall of the gun or vessel, and the gauge was screwed in so that the pressure of the gases could act upon the base of a small piston, which forced a knife edge into a disc of copper. The force required to produce depressions of various depths in the copper was determined by actual trial, and hence the pressure of the gases could be calculated.

Crusher gauge.

The crusher gauge, which is very largely used at the present day, is merely a development of Rodman's gauge, the principal difference being that small cylinders of copper are crushed between two flat surfaces, and from the diminution of height the pressure is deduced. The crusher gauge is shown in Fig. 87: C is the piston; the end next the powder chamber is protected by the gas-check, D, which prevents the gases escaping past it; the copper crusher, A, is held in position by a small spring; the whole is screwed into the wall of the gun. When it is not desired to make a hole in the fire-arm, the pressure in the chamber can be ascertained by placing a small crusher gauge bodily inside the chamber at the back of the charge. On firing, this is thrown out of the muzzle a short distance, and is afterwards picked up and the copper is taken out and measured. Experience has shown that certain precautions are necessary to obtain reliable results: the end of the piston should not be far above the interior surface of the wall of the gun, else the gases in rushing up the empty channel acquire great momentum, which they transmit to the piston, causing the copper cylinder to be crushed too much. The copper should be compressed beforehand with a static pressure only slightly less than that which it is to undergo in the actual test, else the momentum acquired by the piston will in a similar way make the result too high.

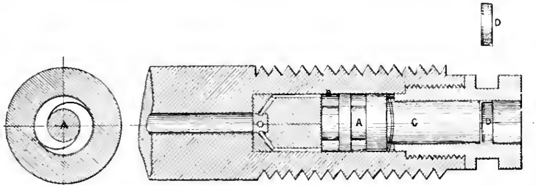

Fig. 87. Crusher Gauge (from *Artillery and Explosives*, by Sir A. Noble)

Rifle pressure.

For measuring the pressures developed by rifle cartridges use is made of a special gun so arranged that, on firing, the base of the cartridge case presses back on a piston, which in turn presses on to the copper cylinder. The cartridge case is dipped beforehand into lubricating oil so that no appreciable amount of force shall be lost by friction.[1]

Shot-gun pressures.

Whereas in rifled fire-arms the chamber pressures are 10 to 20 tons per sq. in., in shot-guns they are generally between 2 and 4 tons per sq. in.: the mechanism can therefore be made lighter and the gas-check can be omitted, but special difficulties are introduced by the great variations which are liable

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[1] This method of testing rifle pressures was introduced by Lt.-Col. Bland Strange.

to occur in the pressures generated by smokeless shot-gun powders, which render it impossible to submit the crusher to a pressure closely approaching that to which it will be subjected. In England lead crushers are generally used instead of those made of copper, these do not require to be pressed beforehand, and they have been found to give satisfactory results. They are standardized by subjecting a proportion of them to an impact test, the diminution of height being ascertained after allowing a standard weight to fall on one from a standard height. The lead crushers are supplied by Eley Bros. By carrying out a large number of simultaneous tests with pistons of different diameters a table has been constructed which is consistent throughout,[1] but the actual values may not be correct; they may require to be multiplied by a factor to give the real number of tons per square inch. The standard diameter of piston now adopted for shot-gun pressure testing is 0·274 inch, giving a sectional area of 1/17 sq. in.[2] On the Continent copper crushers are used.[3]

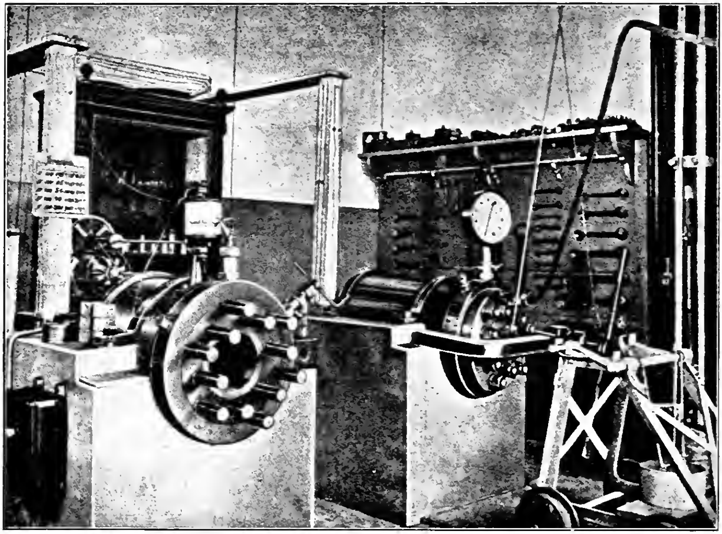

FIG. 88. Bichel's Recording Pressure Gauge

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[1] *Arms and Explosives*, 1914, pp. 7, 24.

[2] *Arms and Explosives*, 1914, pp. 55, 74.

[3] *Arms and Explosives*, 1911, p. 143. *S.S.*, 1911, pp. 395, 421.

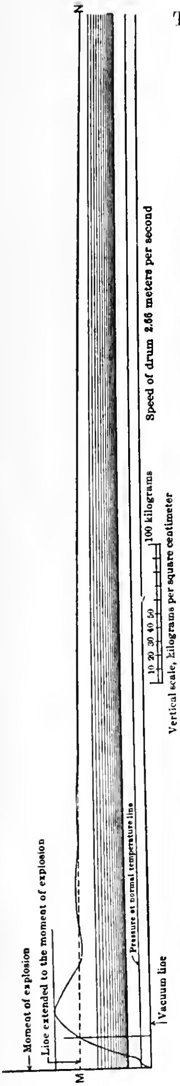

FIG. 89. Indicator Card from Bichel Pressure Gauge (from *Bureau of Mines Bulletin* No. 15)

The study of the pressures generated in fire-arms, together with determinations of the velocities of the projectiles, have rendered possible the enormous advances in the construction of guns and in the manufacture of powders.

Recording pressure gauges.

The crusher gauge can, of course, be used in experiments in closed vessels, as was done by Noble and Abel (*see* Fig. 84), but it only shows the maximum pressure developed, and gives no indication of the time taken to reach this maximum, or the rate of increase in the different parts of the minute fraction of time occupied by the explosion. Various experimenters have therefore carried out tests in which the growth of the pressure was recorded automatically in much the same way as with a steam engine indicator. The pressure acts on a piston which is made to compress a spring and at the same time traces a mark on a drum, which is rotated very rapidly by means of an electric motor.

Noble's.

Sir A. Noble in his experiments on cordite and other propulsive explosives[1] found it necessary, in order to record accurately the maximum pressures developed at high densities of charging, to screw down the spring beforehand, almost to the point corresponding to this maximum. Consequently, the part of the curve indicating the growth of the pressure could not be recorded.

Bichel's.

Bichel for investigating high explosives has used a bomb with a capacity of 15 litres (Fig. 88). In this a charge of 100 or 200 g. is exploded; consequently the density of charging is only 0·013. With black powder this gives a satisfactory diagram, but with high explosives the momentum acquired by the moving parts causes the maximum to be considerably too high, as may be seen in Fig. 89, but the true maximum may be ascertained approximately by extending the line until it meets the normal corresponding to the moment of explosion. The curve gives some indication of the growth of the pressure but not a true measure of it. With such low densities the cooling effect of the walls of the bomb reduces the maximum pressure considerably. In order to eliminate this source

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[1] *Discourse*, Royal Institution, 1900.

of error Bichel uses two bombs of different sizes, and in the larger one he places one large or two small steel cylinders, so as to reduce the volume to 15 litres and at the same time increase the cooling surface. Three different areas are thus obtained with the same capacity. When the maximum pressures are plotted against these areas, the points lie almost on a straight line, and if this be continued until it cuts the normal corresponding to area nil, the theoretical pressure at this density is obtained.

Petavel's recording manometer.

Petavel in his recording manometer greatly diminished the vibration of the spring by making it much stiffer: the motion of the piston is then very small, but it is magnified many times by making it deflect a small mirror, which throws a beam of light on to a piece of sensitized paper wound on a drum, which is rotating rapidly.[1] The manometer is shown in Fig. 90. By means of the thread U the gauge screws into the explosion chamber, the end C of the piston being flush with the inside surface. An air-tight joint is formed by the ring D on the manometer pressing against a flat edge. The end of the gauge from D to E is a good fit in the walls of the explosion chamber, and the joint is thus protected from the direct effect of the explosion. The spring S, about 5 in. in length, is tubular in shape. To prevent buckling it is made to fit the cylinder containing it at two places ϵ_2 and ϵ_2. At the outer end Z it is held by the nut K: at the inner end it is free to move and supports the piston P. As a gas-check there is a leather washer, which is attached to the piston by the screw C and to the fixed part of the gauge by the ring E. The end of the piston projects by about one-hundredth of an inch, and can therefore move back this distance without straining the leather. The motion of the piston is communicated by the rod R to a knife-edge (not shown) facing towards C. A lever is kept pressed against the knife edge by the tension in the wire W, which is stressed almost to its limits of elasticity. The lever is thus enabled to follow the motion of the piston, and by means of a small mirror it records

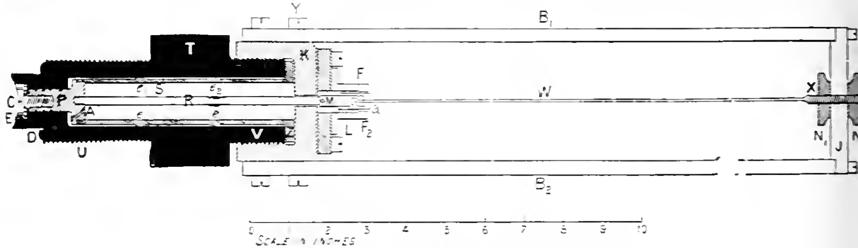

FIG. 90. Petavel's Recording Manometer

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[1] *Phil. Trans.*, vol. 205, 1905, p. 357.

it much magnified on the rotating drum. This recorder has given very satisfactory results. Its time period is sufficiently small to allow records to be obtained not only of the curve of the rise of pressure of the smallest sizes of cordite, but also of the rapid vibrations which modify the curve under certain conditions (*see* Fig. 91, curve 4).

Relation of pressure to density of loading.

At moderate pressures the relationship between the volume, temperature and pressure of a gas is represented with sufficient accuracy by the equation

$$p_1v_1/T_1 = p_2v_2/T_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

or by

$$pv = (t + 273)/273 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where v is the volume occupied at $t°$ and under a pressure of p atmospheres by a quantity of gas, which at 0° and 1 atmosphere has a volume of 1. At high pressures there are considerable divergences from this formula, however, especially in the neighbourhood of the critical temperature. The behaviour of gases is better represented by the equation of van der Waal's

$$(p + a/v^2)(v - b) = (t + 273)/273 \quad . \quad . \quad . \quad . \quad . \quad (3)$$

a and b being constants, varying with each gas, which can be calculated from the critical temperature and pressure. Temperatures of explosion are much higher than the critical temperatures, and it is found that the application of the corrections in equation (3) makes but little difference at pressures up to about 1000 atmospheres and temperatures of 1000° to 2000°, and in view of the many uncertainties attaching to these calculations it is not worth while applying this equation: it is better to adhere to the simpler forms (1) and (2).

At pressures above about 1500 atmospheres the relationship alters somewhat: the term a in van der Waal's equation, which represents the attraction between the molecules brought into play by the diminution of the volume, disappears. The term b, which represents the co-volume or volume actually occupied by the molecules, remains, but assumes a value somewhat smaller than that calculated from the critical data. The variation with temperature also alters. The behaviour of various gases at pressures ranging from 100 to 1000 atmospheres and temperatures from 0° to 200° was investigated by Amagat; and at the ordinary temperature he extended the observations to 3000 atmospheres. The results of his experiments, between 500 and 2000 atmospheres pressure, are represented fairly well by an equation of the form

$$p(v - b) = (t - tk_k)/C \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where t_k is the critical temperature of the gas and C is a constant. The following table gives the values of these terms for the principal gases concerned:

Substance	Critical temperature	From critical data		From high pressure measurements	
	t_k	a	b	b	C
Nitrogen	− 146°	·0027	·0017	·0013	220
Oxygen	− 118°	·0027	·0014	·0011	220
Hydrogen	− 242°	·0004	·0009	·0007	260
Carbon dioxide . .	+ 31°	·0070	·0018	·0012	150
Carbon monoxide. .	− 140°	·0028	·0017	·0012	260
Methane	− 90°	·0037	·0016	·0009	150
Water vapour . .	+ 360°	·0117	·0015	(·001)	(150)

In the case of water there are no direct measurements available at high pressures, and at temperatures well above the critical point, so that the values of b and C can only be estimated by analogy.

At pressures above 2000 atmospheres the co-volume b further decreases, and the equation should apparently be written in the form

$$p(v - b) + p^2c = (t - t_k)/C \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

in which c has a value of about 5×10^{-8}, but the data available are not sufficient to establish the relationship with certainty in the region of these very high pressures.

In calculations of this sort it is, however, more usual to work with an equation of the form

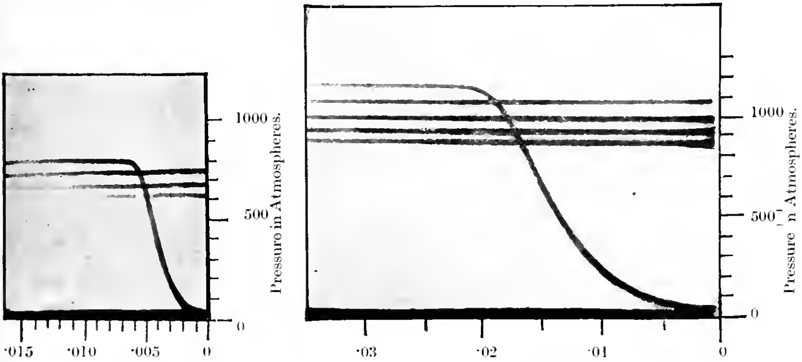
$$p(v - b) = T/K \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

It is often assumed, especially by French workers, that b is equal to one-thousandth of v_0 the volume of the gases measured at 0° and 1 atmosphere. Equation (6) can then be transformed into

$$p = \frac{v_0T}{273(v - \cdot001v_0)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7)$$

where T is the temperature of explosion on the absolute scale and v is the volume within which the explosion takes place, in other words the reciprocal of the density of loading. At high densities this formula gives pressures which are considerably higher than those found by experiment, and it becomes necessary to assume a lower value for the co-volume. Noble and Abel assigned to the co-volume for cordite a value of 0·65 or 0·60 of the weight of the explosive in grammes, and as cordite yields about 890 c.c. of gas and vapour per gramme, these figures correspond to 0·00073 v_0 or 0·00062 v_0. But Noble and Abel's pressure results were not corrected for the cooling effect of the walls of the vessel, although they recognized the existence of this source of error. In the case of cordite Mk.I, Petavel found that the calculated pressures agree satisfactorily with those determined experimentally, if it be assumed that the co-volume is the same as the volume occupied by unit weight of solid cordite at the ordinary temperature, 0·641. At density 0·0744 he found a pressure of 5·137 tons per sq. in., hence T/K in equation (6) is equal to 65·75, p being measured in tons per sq. in.

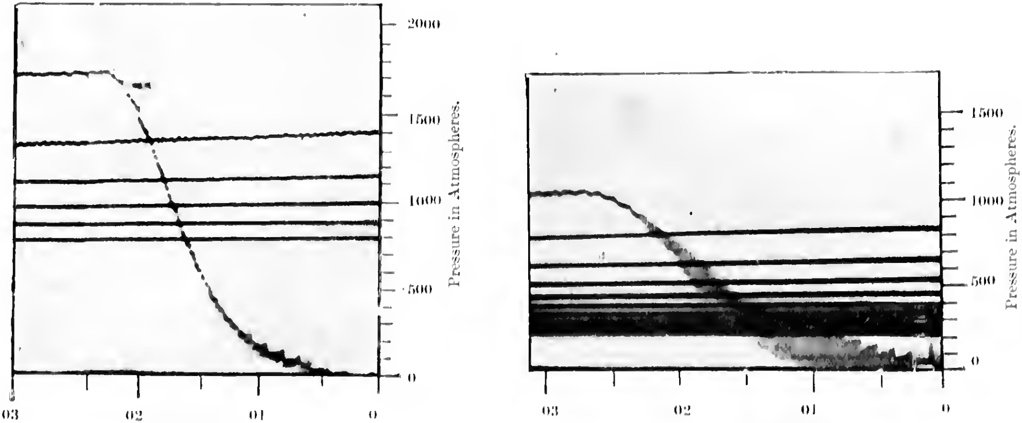
Gravimetric density	Pressure calculated	Determined by Noble	Determined by Petavel
0·05	3·40	3·00	2·87
0·10	7·03	7·10	7·01
0·15	10·91	11·36	11·48
0·20	15·08	16·00	—
0·30	24·42	26·00	—
0·40	35·37	36·53	—
0·50	48·38	48·66	—
0·60	64·10	63·33	—



Time, Seconds
Curve 1.
Cordite, 0·035 inch diameter.
Gravimetric density, 0·0744.
Charge uniformly distributed in spherical enclosure.

Time, Seconds.
Curve 2.
Cordite, 0·175 inch diameter.
Gravimetric density, 0·099.
Charge uniformly distributed in spherical enclosure.

Fig. 91. Curves from Petavel's Manometer



Time, seconds.
Curve 3.
Cordite, 0·175 inch diameter.
Gravimetric density, 0·15.
Charge uniformly distributed in cylindrical enclosure.

Time, Seconds.
Curve 4.
Cordite, 0·175 inch diameter.
Gravimetric density, 0·10.
Charge concentrate in one half of cylindrical enclosure.

FIG. 91 (*continued*). Curves from Petavel's Manometer

It is to be noted, however, that with this value for the co-volume, if the cordite were exploded in its own volume the equation gives an infinite pressure. It is clear, therefore, that with very high densities of loading a still smaller value must be assumed for the co-volume.

If the temperature of explosion be known, and also the total volume of gas, it is possible to make a calculation of the pressure at any density, but it is better to calculate the temperature from the pressure, as the latter can be determined directly, and the former cannot.

Calculation of Temperature

From the heat of explosion.

If the heat generated by the explosion be known, and also the nature and quantities of the products, it is possible to calculate their temperature at the moment of explosion, although it is somewhat doubtful whether the figure thus obtained really corresponds with what actually occurs. In order to make such a calculation it is necessary to know the specific heats of the products, that is, the quantity of heat required to raise the temperature of unit quantity through unit range of temperature. In such calculations it is most convenient to deal with molecular proportions of the products: if the percentage of each substance be divided by its molecular weight and multiplied by 10 it gives the number of "mols" per kg. of explosive. And if this be multiplied by the molecular specific heat it gives the quantity of heat required to raise the temperature of this constituent 1°. The specific heats, unfortunately, are not constant, but increase with rise of temperature, and there are considerable experimental difficulties in determining the specific heats of gases at very high temperatures. Mallard and Le Chatelier estimated them from the pressures generated by gaseous explosions in closed vessels,[1] and arrived at the following results:

Specific heats of gases.

Permanent gases: N_2, O_2, CO, H_2	$4{\cdot}80 + 0{\cdot}0006t$
CO_2, SO_2	$6{\cdot}26 + 0{\cdot}0037t$
Water vapour	$5{\cdot}61 + 0{\cdot}0033t$

These are mean molecular heats at constant volume: when multiplied by the temperature, t, they give the quantity of heat in small calories necessary to raise the temperature from 0° to t°. The total heat required to raise the temperature of the products to t° is given therefore by the equation.

$$Q = At + Bt^2$$

A and B being obtained by multiplying the corresponding values of Mallard and Le Chatelier by the number of mols, adding them together and dividing

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[1] *Compt. rend.*, 1881, p. 1014.

by 1000 to express the result in large calories. Solving the equation for t we have

$$t = \frac{-A + \sqrt{A^2 + 4BQ}}{2B}.$$

The above specific heats have been used by the French authorities for calculating the temperature of explosion of explosives for use in coal-mines. Up to about 1500° these specific heats are probably fairly accurate, but there is considerable doubt as to the values for carbon dioxide and water vapour at higher temperatures. Similar explosion experiments were carried out by Langen,[1] who expressed his results by means of the formulæ:

Carbon dioxide	$6{\cdot}7 + {\cdot}0026t$
Water vapour	$5{\cdot}9 - {\cdot}00215t$

For the permanent gases his values are the same as those of Mallard and Le Chatelier.

More recently Pier has made explosion experiments in a spherical bomb with a capacity of 35 litres.[2] The pressure was measured by means of a corrugated steel diaphragm fixed in the side and carrying a mirror attached half-way between the centre and the circumference. Results were obtained for temperatures from 1300° to 2500°. For lower temperatures up to 1400° values have been obtained by Holborn and Henning at constant pressure by the same method as was used by Regnault for determinations at temperatures up to a few hundred degrees, *i.e.* by passing the gas through a heated tube and then into a calorimeter. From these results and his own, Pier had calculated the following expressions for the mean molecular heats at constant volume between 0° and t°:

Monatomic gases (Argon)	$2{\cdot}977$
Hydrogen	$4{\cdot}700 + {\cdot}00045t$
Nitrogen, oxygen	$4{\cdot}900 - {\cdot}00045t$
CO_2, SO_2	$6{\cdot}800 - {\cdot}0033t - {\cdot}95t^2 \times 10^{-6} - {\cdot}1t^3 \times 10^{-9}$
Water vapour	$6{\cdot}065 + {\cdot}0005t + {\cdot}2t^3 \times 10^{-9}$

Since 1907 gaseous explosions have been under investigation by a Committee of the British Association, which among other subjects has inquired into the specific heats. They maintain that there is an error in the determinations of Regnault and others at constant pressure due to over-correction for conduction of heat along the tube, through which the gases pass to the calorimeter. In consequence of this Regnault's results at moderate temperatures are 2 or 3 per cent. too low, and the error in those of Holborn and Henning is perhaps 7 per cent. Determinations have been carried out by Swann by a different method,

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[1] *Mitteilungen über Forschungsarbeiten auf dem Gebiete des Ingenieurwesens*, Heft 8, 1903.

[2] *Zeits. Elektroch.*, 1909, p. 536; 1910, p. 897.

the gas being heated by means of an electric coil, and the rise of temperature being measured as well as the energy supplied.[1] He thus obtained for air a value of 5·00 at 20°, which is near that calculated from Joly's determination, with a steam calorimeter, which gave 4·96, whereas Regnault's figure was 4·86 and Wiedmann's and Witkowski's were practically the same. For carbon dioxide Swann got 6·93 at 20° and 7·76 at 100°, which again is substantially higher than the older figures. Dugald Clerk has carried out experiments with air in an engine cylinder, and has calculated the specific heat from the curve on the indicator diagram: the mean specific heat between 20° and 120° is calculated to be 5·23. Hopkinson has made similar experiments, in which, however, he has also measured the temperature directly, and has arrived at the value 5·23 over the range 20° to 270°. With gas-engine mixture at a temperature of 1400°, Clerk obtained results in agreement with the specific heats of Langen. Those of Holborn and Henning would be about 8 per cent. lower, and those of Mallard and Le Chatelier several per cent. higher.

The question of specific heats has also been investigated from the purely theoretical standpoint. By means of Planck's Quanten Theory it is possible to calculate from the spectrum of the gas the variation of the specific heat with the temperature. It can thus be shown that the general form of Pier's expression for carbon dioxide is correct, that is to say the specific heat increases rapidly up to about 1000° and then more slowly. In the case of water vapour the increase continues to accelerate up to a very high temperature. Nernst has done much to develop this theory.[2]

The net result is that up to a temperature of about 1500° the specific heats are known approximately; but above this they are still very uncertain, and temperatures of explosion calculated from the heat liberated are of little value. The uncertainty is rendered still greater by an observation of Pier, who attempted to measure the equilibrium of the reaction $CO_2 + H_2 = CO + H_2O$. The results were quite unsatisfactory, and he has suggested that this may have been due to the formation of an endothermic compound of carbon dioxide and water at a high temperature. There is also some uncertainty as to the effect of high temperature combined with high pressure on the specific heats of water vapour and carbon dioxide. Both these substances are liable to dissociate at high temperatures, but to what extent is not known[3]; the amount of dissociation would be diminished by high pressure.

Specific heats of solids.

The specific heats at high temperatures of the solid products of explosion also are not known with certainty. Approximately they follow at ordinary temperatures the law of Kopp: that is to say, the molecular heat of the com-

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[1] *Proc. R.S.*, 1909, A., p. 147.

[2] *See also* Bjerrum, *Zeits. Elektroch.*, 1912, p. 101.

[3] According to K. W. Jurisch 55·7 per cent. of water vapour is dissociated at 2260°. *Zeitsch. Physikal. Chem.* 82, 1913, p. 575.

pound is equal to the sum of the atomic heats of the elements composing it, and the latter, in accordance with the law of Dulong and Petit, mostly have a value of about 6·4. The following have lower values, however: C 1·8, H 2·3, Si 3·8, O 4·0, P and S 5·4. With rise of temperature there always is an increase in the specific heats, but at very high temperatures the rate of increase diminishes. Those elements and compounds, which have low atomic heats at the ordinary temperature, show greater increases with temperature. All the atomic heats seem to approach a constant value of 7 or 8 at high temperatures. For the temperatures concerned in explosive reactions approximately accurate results are probably obtained by assuming that the mean specific heat between 0° and $t°$ increases by 0·0002 of its value at the ordinary temperature for every degree. Thus if S_0 be the specific heat at the ordinary temperature the mean specific heat is $S_0(1 + 0{\cdot}0002t)$.

The specific heats of many of the substances that are liable to occur among the products of explosion are given in Appendix II.

Products of explosion.

If an explosive contain more oxygen than is sufficient to oxidize all the hydrogen to water and the carbon to dioxide, it gives practically the same result in the bomb calorimeter whatever the density of loading, provided that due allowance be made for the detonator or other means of ignition:[1] the heat evolved is the same, as also are the volume and the composition of the gases.

If the explosive do not contain sufficient oxygen for the complete combustion of the hydrogen and carbon, differences are observed when the density is varied: with increase of the density of loading there is considerable increase in the quantity of heat liberated, and a diminution in the total volume of gas. As regards the separate products of explosion, there is a considerable increase in the amount of CO_2 and CH_4, and a diminution in the CO and H_2, and a lesser one in the water.

It is argued by Poppenberg and Stephan[2] that at the moment of explosion the composition of the products is the same, whatever the density of loading, and consequently the heat of explosion is also the same. The differences found are ascribed to reactions taking place during the cooling of the products. When the density is high, there is a larger quantity of heat to be conducted away through the same cooling surface, consequently the time of cooling is longer, and the secondary reactions proceed further. There is no doubt much truth in this contention: it may not be strictly accurate in the case of propulsive explosives, because with them the time of explosion is comparatively long, and secondary reactions must take place in some portion of the products before the whole of the powder is consumed. With detonating explosives the course of the change is no doubt different, but from the study of the explosion of gaseous mix-

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[1] *See S.S.*, 1907, p. 306.

[2] *S.S.*, 1909, pp. 281, 305; and 1909, p. 388; 1910, pp. 266, 291, 310, 452, 474. *See also* Kast, *S.S.*, 1910, pp. 205, 248, 376, 399.

tures there is reason to think that the products formed in the wave of detonation are not necessarily those which are most stable at the temperature of explosion. The change takes place therefore in three stages: first, certain products are formed in the detonation wave, then almost instantaneously other reactions take place so that an equilibrium is set up corresponding to the temperature of explosion: at this very high temperature the reactions proceed with enormous velocity. Finally, as the temperature falls the composition corresponding to stable equilibrium gradually changes: at first the composition of the gases follows very closely the equilibrium composition, but as the temperature gets lower, it lags behind more and more until the velocity of change becomes negligible.

One of the reactions that takes place as the temperature falls is:

$$CO + H_2O = CO_2 + H_2 + 10{\cdot}1 \text{ Cals. (water, gas).}$$

If the water be liquid, there is instead a negative production of heat of $-0{\cdot}4$ cals., so that the actual thermometer reading in the calorimeter is practically unaffected and, even when the result has been corrected for the condensation of water, the effect is not great. The total volume of gas is also unaffected by the reaction, as there are two molecules on each side of it. The reaction is not a complete one, but tends towards an equilibrium, which shifts with the temperature. At any temperature the relation $(CO)\ (H_2O)/(CO_2)(H_2) = k$ is constant, whatever the actual quantities of the different gases. From various thermo-dynamical data, Haber[1] has calculated that the relation of k to the absolute temperature is given by the equation:

$$\log k = -2116/T + 0{\cdot}783 \log T - 0{\cdot}00043\ T$$

the logarithms being common ones. The equation has been confirmed by experiments with gas flames. If $T = 2000°$ $k = 4{\cdot}61$, and if $T = 3000°$ $k = 5{\cdot}31$. Poppenberg and Stephan prefer, however, to take $k = 7$ about, for the temperature of explosion, this figure being deduced from calculations by Langen and others. But this difference only diminishes the calculated heat of explosion by quite a few calories.

Formation of methane.

A reaction that affects the results considerably more is the formation of methane. Poppenberg and Stephan consider that no methane exists at the moment of explosion, but that it is formed, as the gases cool down, by the action of the hydrogen on the oxides of carbon, or on carbon itself if there be any present. In support of this view they have shown experimentally that if powder gases be kept in contact with a Nernst light, a considerable percentage of methane is formed. If picric acid or trinitro-toluene be detonated in a bomb in the ordinary way there is much methane, especially at high densities of loading, but if they be detonated in their own volume in a small block placed

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[1] Thermodynamik der technischen Gasreaktionen.

inside a bomb, there is not more than 0·5 per cent. Under these circumstances the gases are cooled very rapidly in consequence of the work done in destroying the block, and little time is afforded for the formation of methane. Moreover it has been shown by Mayer and Altmayer [1] that methane cannot exist at a very high temperature. The formation of methane is represented by the equations:

$$CO + 3H_2 = CH_4 + H_2O + 50{\cdot}7 \text{ Cals.}$$
$$CO_2 + 4H_2 = CH_4 + 2H_2O + 40{\cdot}6 \text{ Cals.}$$

However it may be produced, for every volume of methane the total volume of gas is reduced by two volumes, and the heat is increased. With an increase in the proportion of hydrogen the formation of methane is greatly accelerated: the formation is proportional to the cube or the fourth power of the concentration of the hydrogen. Hence trinitro toluene, which gives much hydrogen on detonation, is liable to give also much methane.

Of ammonia. The same conditions also favour the formation of ammonia $2NO + 5H_2 = 2H_2O + 2NH_3$, whereas if there be only a moderate amount of hydrogen, the reaction is mostly in accordance with the equation $2NO + 2H_2 = 2H_2O + N_2$. Poppenberg and Stephan found considerable quantities of ammonia when trinitro-toluene and dinitro-benzene were detonated in their own volume and made to do work, so apparently it is formed at a high temperature.

Carbonates.

Carbon.

If the explosion produce a solid residue, further complications are introduced. Metallic oxides are generally converted into carbonates and bicarbonates, and in making the calculations it is necessary, therefore, to allow for the carbon dioxide thus combined, and for the heat produced. Some explosives leave a residue of carbon. Thus Poppenberg and Stephan [2] found that picric acid, detonated in a lead block inside a bomb, gave 6 per cent. of carbon. The amount, however, depends on the violence of the detonation, for if a very powerful primer be used there is much carbon. But if the gases cool gradually in contact with the carbon, the latter is acted on by the water vapour, as in the production of water gas: $C + H_2O = CO + H_2 - 28{\cdot}3$ Cals. The temperature is reduced by this reaction and the volume of gas increased. It was found that according to the circumstances the following percentages of carbon could be recovered from the residues of detonation:

	In lead block (Doing work)	In bomb $\Delta = {\cdot}02$
Picric acid	6·0 per cent.	0·29 per cent.
Trinitro-toluene . . .	17·2 ..	4·82 ..
Dinitro-benzene . . .	19·37 ..	—

At higher densities detonation in the bomb would have given still lower percentages.

Aluminium. The effect of aluminium is somewhat similar: it is added generally in the form of a fairly coarse powder, partly in order to retard its oxidation during

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[1] *Ber.*, 40 1907, p. 2134.

[2] *S.S.*, 1910, p. 294.

storage. It cannot take part very largely in the original explosive reaction, but afterwards it reduces the water and carbon dioxide with the production of much heat :

$$2Al + 3CO_2 = Al_2O_3 + 3CO + 176{\cdot}4 \text{ Cals.}$$
$$2Al + 3H_2O = Al_2O_3 + 3H_2 + 206{\cdot}5 \text{ Cals.}$$

When ammonal was detonated in a porcelain block, Poppenberg and Stephan found that a considerable proportion of the aluminium remained unoxidized. There was also 3·36 per cent. of methane in the gases and 2·62 per cent. of other hydrocarbons, mostly acetylene, whereas when the ammonal was exploded in a bomb in the usual way at a density of 0·02, the percentage of acetylene was only 0·2 to 0·6 per cent. They consider that in this case, as also in that of dinitro-benzene, the methane is not formed directly, but acetylene is first produced from carbon monoxide and hydrogen at a high temperature :

$$2CO + 3H_2 = HC : CH + 2H_2O$$

and the methane is formed from this.

Will has given the following figures for a number of explosives : [1]

	Heat generated Cals./Kg.	Gas evolved Litres/Kg.	Calculated Temperature
Blasting gelatine	1640	710	3540° C.
Nitro-glycerine	1580	712	3470
Nitro-mannite	1520	723	3430
Dynamite No. 1	1290	628	3160
Nitro-glycerine powder (40 per cent.)	1290	840	2900
Guncotton (13 per cent. N)	1100	859	2710
Guncotton powder	900	830	2400
Collodion cotton (12 per cent. N)	730	974	1940
Ammonium nitrate explosive (10 per cent. mono-nitro-naphthalene)	930	925	2120
Picric acid	810	877	2430
Black powder	685	285	2770
Ammonium nitrate	630	937	2120
Mercury fulminate	410	314	3530

Calculation of temperature from pressure.

If we know the pressure p which the explosive gives when it is fired in a capacious bomb of volume v, and also v_0 the volume of the gases and vapours reduced to 0° and 1 atmosphere pressure, the temperature of explosion can be calculated very easily. But p should be corrected for the cooling effect of the walls of the bomb.

$$T = 273\, pv/v_0$$
$$t = 273\, pv/v_0 - 273$$

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[1] *Z. f. Elektroch.*, 1906, 558. Brunswig, *Explosives*, pp. 13, 152.

Direct measurement of temperature.

Macnab and Ristori proposed to measure the temperatures generated by propellent explosives by the use of a series of thermocouples of various thicknesses. From the results they intended to estimate what current would be obtained. if the wires of the thermocouples were of negligible thickness, and hence to calculate the temperatures.[1] The temperatures might perhaps be measured by means of an optical pyrometer in much the same manner as was done by Borland in the case of percussion caps (*see* p. 520).

EXAMPLES OF CALCULATIONS

Hall and Howell [2] have made some experiments with an explosive having the following composition :

Component	Formula	Per cent.	Molecular weight	Mols per kg.	Heat of formation		Ultimate composition Gramme-atoms			
					Molecular	Total	C	O	N	H
Ammonium nitrate	$N_2H_4O_3$	89·08	80·1	11·12	88·05	979·2	—	33·36	22·24	44·48
Trinitro-toluene .	$C_7H_5N_3O_6$	6·57	227·2	0·29	10	2·9	2·06	1·74	·87	1·45
Nitro-naphthalene	$C_{10}H_7NO_2$	4·19	173·1	0·24	−13·8	−3·2	2·42	·48	·24	1·70
Moisture . .	H_2O	0·17	18·0	0·09	68·4	6·4	—	·09	—	·18
		100				985·3	4·48	35·67	23·35	47·81

Product	Per cent.	Molecular weight	(2) × (3)	Mols per kg.	Heat of formation		Ultimate composition Gramme-atoms			
	(2)	(3)	(4)	$(2)\frac{559·5}{3239}$	Molecular	Total	C	O	N	H
CO_2 . . .	26·7	44·0	1173	4·610	97·0	447·2	4·61	9·22	—	—
O_2 . . .	3·2	32·0	102	·553	—	—	—	1·11	—	—
N_2 . .	70·1	28·0	1964	12·105	—	—	—	—	24·21	—
	100		3239	17·268						
Gases . .	55·95									
H_2O . .	43·03	18·0		23·90	68·4	1634·8	—	23·90	—	47·80
O (as SnO_2) .	1·02	16·0	(SnO_2	·32)	141	45·1	—	·64	—	—
	100			41·17		2127·1 985·3	4·61	34·87	24·21	47·80
						1141·8				
Correction to constant volume, 17·3 × 0·58						10·0				
						1151·8				

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[1] *Proc. Roy. Soc.*, 66, p. 221.

[2] *U.S, Bureau of Mines Bulletin* 15,

Of this, 100 grammes were fired in a Bichel calorimeter by means of a No. 7 detonator. In three experiments the number of Calories found per kg. after deducting 8·6 Cals. for the detonator were 1208, 1211, and 1171, mean 1197. Two hundred grammes wrapped in 7·6 grammes of tin-foil were also fired in a Bichel pressure gauge. The products of explosion were found to consist of 111·9 grammes of gas having the composition given below and 84·2 grammes of water. Of the loss it may be assumed that 2·04 grammes of oxygen were consumed in converting the tin-foil into oxide of tin, and the remaining 1·86 grammes were water. Then we have the products of explosion (*see* Table at bottom of page 460). The heat calculated from the analyses, 1152 Calories, is somewhat less than that found. The agreement in the elementary composition is not very good either. If now the heat be calculated from the analysis of the explosive on the assumption that part of the defective oxygen has been consumed in converting the tin-foil into tin oxide and the remainder of it has formed a thin layer of iron oxide in the interior of the bomb, we have for the products:

Product	Mols per kg.	Heat of formation	Calories
CO_2	4·48	97·0	434·6
O_2, N_2	12·23	—	—
H_2O	23·90	68·4	1634·8
SnO_2	·32	141·0	45·1
Fe_3O_4	·25	271·0	67·7
			2182·2
			985·3
			1196·9 + 10·0 = 1206·9

It is noticeable that the third determination of the heat of explosion gave results considerably below the first two. This may have been due to the formation of a protective coat of oxide on the surface of the steel. Eliminating the third result, the mean of the other two is 1209·5, agreeing well with the above. As the gaseous products of the detonator are not included in this calculation, no allowance is to be made on this account.

In calculating the temperature of explosion in the pressure bomb it is necessary to take into account the products of the detonator. To 200 grammes of explosive there are 1·275 g. fulminate of mercury, 0·225 of the chlorate of potassium and about 3 g. of metallic copper. The following Table gives the number of mols per kg. of the various solid products and the molecular specific heats at the ordinary temperature:

Product	Mols per kg.	Molecular Specific Heat	Calories
SnO_2	0·32	14·0	4·48
Cu	0·24	5·8	1·39
Hg	0·02	6·6	·13
KCl	0·01	12·6	·13
Fe_3O_4	0·25	36·5	9·12
			15·25

Strictly speaking, the mercury should be considered as vapour, but the amount is so small, that it is not worth while making the necessary additional calculations, but if only a few grammes of explosive be used, this correction should be made. The detonator also produces 0·045 mol of CO_2 and 0·022 of N_2, but requires 0·009 mol of O_2 to complete the oxidation of the carbon. Hence we have, using Mallard and Le Chatelier's specific heats :

Product	Mols per kg.	Molecular Heat	Calories per °C.
CO_2 . . .	4·52	$6{\cdot}26 + {\cdot}0037t$	$28{\cdot}29 + {\cdot}0168t$
O_2, N_2 . . .	12·24	$4{\cdot}80 + {\cdot}0006t$	$58{\cdot}75 + {\cdot}0073t$
H_2O . . .	23·90	$5{\cdot}61 + {\cdot}0033t$	$134{\cdot}08 + {\cdot}0789t$
Solids . . .	—	$15{\cdot}25 + (1{\cdot}0002t)$	$15{\cdot}25 + {\cdot}0030t$
	40·66		$236{\cdot}37 + {\cdot}1060t$

The heat of explosion requires to be corrected for the heat of condensation of the water vapour, and the heat due to the detonator must be added on again, but only half the amount, as twice as much explosive was used in the pressure bomb :

$$1197 - 23{\cdot}9 \times 10{\cdot}4 + 4{\cdot}3 = 952{\cdot}7 \text{ Cals.}$$

$$t = \frac{-\,{\cdot}2364 + \sqrt{({\cdot}2364^2 - 4 \times {\cdot}000106 \times 953)}}{2 \times {\cdot}000106} = 2037^\circ$$

Using Pier's specific heats we have :

CO_2 . . .	$4{\cdot}52(6{\cdot}800 + {\cdot}0033t - {\cdot}95t^2 \times 10^{-6} + {\cdot}1t^3 \times 10^{-9})$
N_2, O_2 . . .	$12{\cdot}24(4{\cdot}900 + {\cdot}00045t)$
H_2O . . .	$23{\cdot}90(6{\cdot}065 + {\cdot}0005t - 2t^2 \times 10^{-6} + {\cdot}2t^3 \times 10^{-9})$
Solids . . .	$15{\cdot}25(1 + {\cdot}0002t)$
Total . . .	$250{\cdot}9 + {\cdot}0246t - 4{\cdot}29t^2 \times 10^{-6} + 5{\cdot}23t^3 \times 10^{-9}$

Assuming a temperature of 2600°, this gives $t = 2521°$. Assuming next a temperature of 2550°, we get $t = 2560°$, which may be taken as the temperature by this method.

From pressure

The following pressures were recorded with Bichel gauges arranged with different cooling surfaces, the charge being 200 grammes and the volume of the gauges 15 litres :

Cooling surface	Pressure at time 0 from indicator card Kilogrammes per sq. cm.			Mean
3914 sq. cm.	110·63	107·50	105·63	107·92
6555 ,,	100·00	100·00	98·75	99·58
7624 ,,	95·63	95·00	98·75	96·46

Hence it is calculated that with no cooling surface the pressure would be 119·92 kg./cm.^{2} equal to 116·0 atmospheres. The volume of gas at 0° and 1 atmosphere is given by the number of mols of gas multiplied by 22·41. Hence we have :

$$T = \frac{116 \times 15 \times 273}{40{\cdot}66 \times 22{\cdot}41 \times 0{\cdot}2} = 2606$$

$$t = 2606 - 273 = 2333°$$

The agreement with the temperature as calculated with Pier's specific heats is not satisfactory, although these are based on the pressures developed by the explosion of gas mixtures, and recorded by a gauge somewhat similar to that of Bichel. The fault may lie partly with the Bichel gauge, the moving parts of which are heavy, and not sufficiently rigid, with the result that the pencil oscillates violently during the first hundredth of a second (*see* Fig. 85). The pressure at the moment of explosion has been deduced from the subsequent pressures on the assumption that the rate of cooling is uniform : but this is not the case, for the surfaces are originally cold and take up heat at first much more rapidly than they do when they have become warm. An inspection of Petavel's results shows that the early part of the pressure curve resembles a parabola more than a straight line. It is possible, therefore, that the pressures have been under-estimated somewhat. Another cause for the discrepancy is the anomalous behaviour of mixtures of water vapour and carbon dioxide at high temperatures, possibly due to the formation of an endothermic compound. The true temperature of explosion is possibly somewhere between 2350° and 2550°.

If the explosive contain alkali nitrates, it is necessary to take into account the formation of bicarbonates, and if the oxygen be insufficient for complete oxidation, other complications are introduced. Another explosive examined by Hall and Howell had the composition :

Component	Formula	Per cent.	Molecular weight	Mols per kg.	Heat of formation		Ultimate composition Gramme-atoms			
					Molecular	Total	C	O	H	N
Nitro-glycerine .	$C_3H_5N_3O_9$	29·92	227	1·098	94·2	103·4	3·29	9·88	5·49	3·29
Saltpetre . .	KNO_3	25·37	101	2·512	119	298·9	—	7·64	—	2·51
Barium nitrate .	BaN_2O_6	4·42	261	·169	227·2	38·4	—	1·01	—	·34
Wood-meal .	$C_{50}H_{72}O_{33}$	34·60	1200	·288	1500	432·4	14·41	9·51	20·76	—
Starch . .	$C_6H_{10}O_5$	6·64	162	·410	225·9	92·6	2·46	2·05	4·10	—
Moisture . .	H_2O	4·05	18	2·250	69·0	155·2	—	2·25	4·50	—
		100				1120·9	20·16	32·34	32·85	6·14
Products of detonator							·08	·14	—	·08
							20·24	32·38	34·85	6·22

In the pressure bomb 200 grammes fired with a No. 7 detonator gave 130·3 g. of gas, 37·3 g. of soluble solid (potassium bicarbonate), 11·7 g. of insoluble solid (barium carbonate) and 12·4 g. of water. The loss was therefore 8·3 g., or allowing for the non-metallic products of the detonator 8·76. g. The figures for the solid products do not agree at all with the analysis of the explosive, which would give 50·24 g. of potassium bicarbonate and 6·72 of barium carbonate. Assuming that the latter figures are the more correct, and that a little water was lost as well as a portion of the solids, we have :

Product	Per cent. by volume	Molecular weight	Proportions by weight	Mols per kg.	Heat of formation		Ultimate composition Gramme-atoms			
					Molecular	Total	C	O	H	N
CO_2 . . .	18·9	44	832	5·41	94·3	510·2	5·41	10·82	—	—
CO . . .	36·3	28	1016	10·39	26·1	271·2	10·39	10·39	—	—
H_2 . . .	29·1	2	58	8·33	—	—	—	—	16·66	—
CH_4 . . .	5·8	16	93	1·66	18·6	30·9	1·66	—	6·64	—
N_2 . . .	9·9	28	277	2·83	—	—	—	—	—	5·66
	100		2276	28·62						
Gases	65·15									
$KHCO_3$ . .	25·12	100	—	2·51	233·3	586·0	2·51	7·54	2·51	—
$BaCO_3$ . .	3·36	197	—	·17	282·5	47·7	·17	·51	—	—
H_2O . . .	6·83	18	—	3·80	69·0	362·2	—	3·80	7·60	—
	100·46					1708·2 1120·9	20·14	33·06	33·41	5·66
						587·3				

To this must be added 28·62 × 0·58 Cals. to correct to constant volume, and about 1·2 Cals. are to be subtracted for the partial solution of the potassium bicarbonate, which brings the result to 602·7 Cals.

The heat of explosion as determined directly in the calorimetric bomb was in three experiments: 575, 567 and 570 Calories, mean 570·7, to which must be re-added 4·3 for the detonator, making it 575, as compared with 602·7 Calories by calculation from the analyses. Berthelot's heats of formation have been used in the calculations.

In calculating the state of the products at the moment of explosion it is necessary to convert all the potassium bicarbonate to carbonate and the liquid water into vapour. The former change proceeds in accordance with the equation: $2KHCO_2 = K_2CO_3 + CO_2 + H_2O - 35{\cdot}4$ Cals. (water gas), and the vaporization of the water at 18° absorbs 10·5 Cals., according to Winkleman's formula. On the other hand 1·2 Cals. are to be added on account of the bicarbonate being no longer in solution: $575 - 17{\cdot}7 \times 2{\cdot}51 - 3{\cdot}80 \times 10{\cdot}5 + 1{\cdot}2 = 491{\cdot}9$ Cals. By the reconversion of the methane the available heat is further reduced: $CH_4 + H_2O = CO + 3H_2 - 50{\cdot}7$ Cals., $491{\cdot}9 - 1{\cdot}66 \times 50{\cdot}7 = 407{\cdot}7$ Cals. The Total number of mols of gas after making these corrections is 38·26.

The pressure generated by 200 grammes in a 15-litre bomb corrected for surface cooling was 67·0 kg./cm.^{2} equal to 64·85 atmospheres. Hence the temperature as calculated from the pressure is

$$T = \frac{64{\cdot}9 \times 15 \times 273}{38{\cdot}26 \times 22{\cdot}41 \times 0{\cdot}2} = 1549$$

$$t = 1276^\circ$$

At this temperature the equilibrium constant $k = (CO)\,(H_2O)/(CO_2)(H_2) = 2{\cdot}8$, and it is necessary to adjust the quantities of the different gases accordingly. These various changes are shown in the following Table:

Product	Original Analysis	Correction for		Result	Corrected to $k = 2{\cdot}8$
		Bicarbonate	Methane		
CO_2 . . .	5·41	+ 1·26	—	6·67	3·51
CO	10·39	—	+ 1·66	12·05	15·21
H_2	8·33	—	+ 4·98	13·31	10·15
H_2O . . .	3·80	+ 1·26	− 1·66	3·40	6·56
N_2	2·83	—	—	2·83	2·83
CH_4. . . .	1·66	—	− 1·66	—	—
$KHCO_3$ . . .	2·51	− 2·51	—	—	—
K_2CO_3 . . .	—	+ 1·26	—	1·26	1·26
$BaCO_3$ . . .	·17	—	—	·17	·17

The last change involving 3·16 mols of each of the gases reduces the heat available by 3·16 × 10·1 Cals., and brings it to 375·8 Cals. The calculation of the temperature with Mallard and Le Chatelier's specific heats is as follows:

	Mols	Specific Heat		
Solids				
K_2CO_3	1·26 ×	28·4 =	35·78	
$BaCO_3$	·17 ×	21·8 =	3·71	
Sn	·32 ×	6·5 =	2·08	
Cu	·24 ×	5·8 =	1·39	
Hg	·02 ×	6·6 =	·13	
KCl	·01 ×	12·6 =	·13	
			43·22 × (1 + ·0002t) =	43·2 + ·0086t
Gases				
CO, H_2, N_2			28·19 × (4·80 + ·0006t) =	135·3 + ·0169t
CO_2			3·51 × (6·26 + ·0037t) =	22·0 + ·0130t
H_2O			6·56 × (5·61 + ·0033t) =	36·8 + ·0216t
				237·3 + ·0601t

Hence it is calculated $t = 1222°$.

The agreement is not very close: Mallard and Le Chatelier's specific heats may be somewhat too high even at this comparatively low temperature. On the other hand, there may have been some formation of methane before the pressure gauge registered. Over-correction for methane would reduce the temperature as calculated from the pressure, but would reduce that calculated from the heat about four times as much. The actual maximum temperature attained in the bomb may be estimated roughly at 1300°.

CHAPTER XXX

POWER AND VIOLENCE OF EXPLOSION

Power of explosives : Trauzl test : French method : Earth test : Concrete test : Ballistic pendulum : The time factor : Mettegang recorder : Dautriche's method : Velocity of sound : Influence of density : Influence of diameter : Of envelope : Of primer : Of temperature : Velocity of detonation of nitro-glycerine : Of nitro-glycerine explosives : Of sundry explosives : Brisance : Tests under water.

Power of explosives. In the last chapter methods were dealt with for the determination and calculation of the temperature, pressure and volume of the products of explosion. These three quantities are interdependent, so that if we know two of them, we should be able to calculate the third ; we could do this with certainty if we were better acquainted with the behaviour of the products at these high temperatures and pressures. If the explosion take place at a fairly low density, the relationship is given by the equation : $pv/\mathrm{T} = p_0 v_0/273$, where p is the pressure of explosion in atmospheres and T is its absolute temperature, v is the volume of the vessel in which the explosion takes place, and v_0 is the specific volume of the gaseous products from unit weight of explosive calculated to 0°C. and the standard pressure p_0.

If f be put to pv, the above expression may be transformed into

$$f = pv = \frac{v_0 \mathrm{Q}}{c} \times \frac{p_0}{273} + \frac{p_0 v_0 \mathrm{T}_1}{273}$$

where Q is the quantity of heat set free by the explosion of unit weight, and c is the sum of the mean specific heats of the products, a very uncertain quantity, and T_1 is the temperature of the explosive before it is fired. The quantity f is called by French writers the " pression specifique " or " force specifique " or simply " force " of the explosive. It is the pressure per unit area that would be obtained by the explosion of unit weight in unit volume if the ordinary gas laws were applicable at this density. It is usually expressed by them in kg. per sq. cm. exerted by the explosion of 1 g. in a volume of 1 c.c. They generally calculate f from various theoretical assumptions ; more rarely they determine it by actual experiment. According to the kinetic theory of gases the kinetic energy of the explosion gases is equal to 1·5 f.

Berthelot has given to the expression $v_0\mathrm{Q}/c$ the name of " characteristic product,"[1] and used it as a measure of the power of the explosive. But in consequence of the difficulty of ascertaining the value of c, the product v_0Q has often been used instead. It is preferable, however, both on theoretical and practical grounds to use the other side of the above equation, and measure the strength of the explosive by the product pv. It is true that v_0 and Q can be measured or calculated without any great difficulty, but they require to be corrected for various changes that take place during the cooling of the gases, and the exact magnitude of the corrections is by no means certain. On the other hand p can be determined in a pressure bomb, such as that of Bichel, and only requires to be corrected for the cooling action of the surface, and the measurements in the instrument itself supply this correction. The volume of the bomb, v, is of course easy to ascertain and is constant. For one and the same instrument and weight of charge the power of the explosive may be taken as proportional to the pressure developed.

In a series of experiments carried out by Bichel in 1902[2] the pressures found were nearly proportional to the results obtained in the Trauzl lead block, but the product v_0Q did not show the same degree of regularity:

	v_0 Lit. kg	Q Ca., kg.	$\frac{v_0Q}{1000}$	p	Trauzl Test
Blasting gelatine	851	1422	1210	70·4	650
Gelignite 65 per cent.	487	1321	643	55·4	560
Dynamite No. 1	536	1170	627	48·2	520
Donarite	1023	836	856	48·7	500
Ammon-carbonit I	922	850	782	46·8	470
Ammon-carbonit	930	757	703	42·2	330
Thunderite	1021	777	794	38·0	310
Carbonit II	746	602	448	34·7	300
Carbonit I	773	601	464	32·4	290
Kohlen-carbonit	816	506	412	31·0	270
Carbonite	729	576	420	26·6	265
Gunpowder	386	574	228	18·7	108

The pressures are in kilogrammes per square centimetre developed by 100 g. in a 15-litre chamber after elimination of the surface influence. Bichel obtained no result with gunpowder in the lead block, using ordinary stemming: the value given above was obtained by Tschokke, who stemmed it with Portland cement.

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[1] Produit caractéristique, *see Force des Matières explosives*, vol. i. p. 64: *Explosives and their Power*, p. 32.

[2] *Testing Explosives*, Table I.

If Q be multiplied by the mechanical equivalent of heat, 425, it gives W the maximum quantity of work that can possibly be done by unit weight of the explosive

$$W = 425Q$$

It is called by French writers the *potential* of the explosive and is usually expressed in kg.-metres per kg. of explosive. Also if p be expressed in kg. per sq. metre for 1 kg. exploding in 1 cubic metre and then be multiplied by $1\frac{1}{2}$, the kinetic energy of the gaseous products of combustion is found. These calculations have been carried out for the above explosives, the results being expressed for convenience in kg.-metres per 1 g. of explosive :

	Total energy W	Kinetic energy $1{\cdot}5pv$
Blasting gelatine	604	158
Gelignite 65 per cent.	561	125
Dynamite No. 1	497	108
Donarite	355	110
Ammon-carbonit I	361	105
Ammon-carbonit	322	95
Thunderite	330	86
Carbonit II	256	78
Carbonit I	255	73
Kohlen-carbonit	215	70
Carbonite	245	60
Gunpowder	244	42

Trauzl test.

Trauzl's lead block test affords a ready means of ascertaining the approximate relative strength of explosives. It consists in firing a charge of the explosive in a hole in a block of lead and measuring the size of the cavity formed. At the Fifth International Congress of Applied Chemistry, held at Berlin in 1903, standard conditions were laid down for carrying out the test :

" *The lead cylinder* is 200 mm. in height and 200 mm. in diameter. In its axis is a hole 125 mm. deep and 25 mm. in diameter to take the charge. The purest refined soft lead should be used, and for comparative trials the cylinders should all be from one melting. The sketch (Fig. 92) shows a convenient form of mould for casting the blocks. In order to pre-heat the mould, a red-hot ring is placed round it.

" *The Process.* The blocks should be allowed to stand after casting sufficiently long to attain a uniform temperature of 15° to 20°. Ten g. of the explosive are weighed out and wrapped in a piece of tin-foil, of 80 to 100 g. per sq. metre, of the dimensions shown at the bottom of Fig. 92, so as to form a cartridge of 25 mm. diameter. An electric detonator containing a charge of 2 g. is inserted into the centre of the cartridge. The cartridge is carefully pressed home with a wooden rod keeping the wires central. For tamping, sharp dry quartz sand is used, which passes through a sieve of 144 meshes per sq. cm. (30 meshes to the inch), the wire being 0·35 mm. thick. The sand is run in until the hole is full, and the excess is removed. The charge is then fired electrically. Afterwards the lead block is inverted and any residue is removed with a brush. The quantity of water is then ascertained that is required exactly to fill the cavity. This, less the original volume of the hole, gives a measure of the power of the explosive.[1]

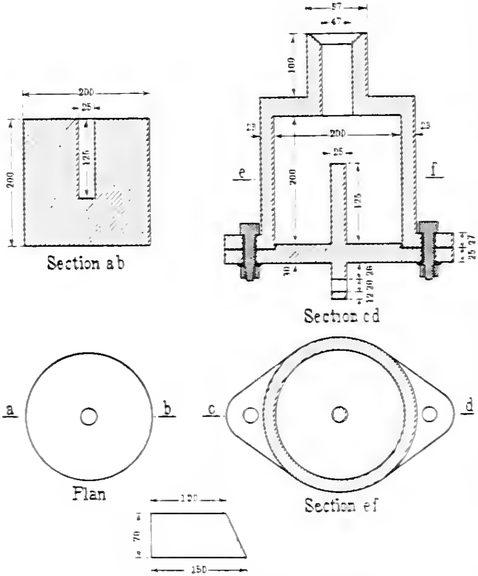

Fig. 92. Trauzl Lead Block Test

“*Interpretation of the Results.* (1) Lead block tests can only claim to give satisfactory comparative results when they are made with the same class of high explosive. If there be great differences in the speed with which the pressure develops, the results are no longer comparable.

“(2) Statements as to the strength of explosives should always be based on at least three determinations.

“(3) The reliability of the test is affected considerably: (*a*) By the uniformity of the temperature of the lead at the time of the test. The standard temperature is 15° to 20° C.; (*b*) by the uniformity of the tamping; (*c*) by the uniformity of the test.”

The lead block test has the advantage that it imitates fairly closely the

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[1] The enlargement caused by a detonator alone under the same conditions is also deducted sometimes.—A. M.

conditions in a bore-hole, only unfortunately the charge has to be small. The warning against using the test for the comparison of explosives with different velocities of detonation appears to be unnecessarily emphatic, for both Kast [1] and Dautriche [2] have found that the results are unaffected by considerable variations in the density to which explosives are compressed, although this has a very great influence on the velocity of detonation. In the case of non-detonating explosives, such as black powder, the test fails, however, as the tamping is blown out before the full pressure is developed, or the gases escape through it, unless a more resistant tamping material be used, such as Portland cement. Probably the results are affected more by the temperature of explosion, the lead on the interior surface being eroded by the hot gases. For this reason aluminium explosives, which produce very high temperatures, give unduly high results in the lead block. If the lead blocks were weighed before and after the test, and the results corrected for the quantity of metal eroded away, it is possible that the figures would be more satisfactory.

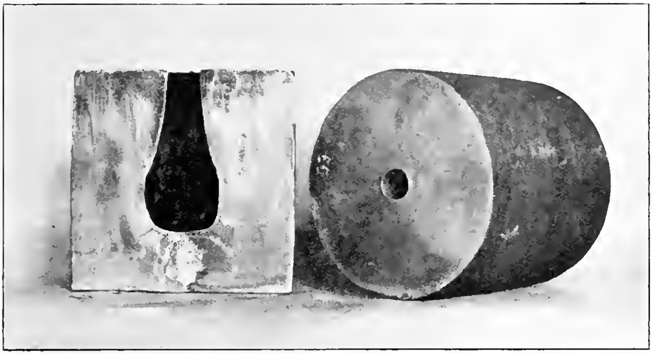

Fig. 93. Trauzl Lead Block after Test, and Section showing Expansion of Cavity by Explosive (from *Bureau of Mines Bulletin*, No. 15)

Neumann gives the following as typical results with the Trauzl test: [3]

Nitro-glycerine	540 c.c.
Blasting gelatine	530 c.c.
Gelignite	420 c.c. (65 N G, 25 $NaNO_3$, 8 W.M.)
Gesteins-Westfalit	380 c.c. (Ammonium nitrate exp.)
Picric acid	315 c.c.
Trinitro-toluene	290 c.c.
Safety gelatine dynamites	200–300 c.c.

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[1] *Spreng- und Zündstoffe*, p. 1030.

[2] *Compt. rend.*, 144, 1907, p. 1032; *S.S.*, 1907, p. 313.

[3] *Ang.*, 1911, p. 2231.

Some of the modern safety explosives have been so far diluted to meet the requirements of the gallery tests, however, that they enlarge the cavity less than 200 c.c.

French method.

In France the Trauzl test is carried out somewhat differently.[1] The dimensions of the lead block are the same. The explosive is placed carefully in the hole, the height that it occupies is measured, and the density is calculated. A detonator containing 1·5 g. fulminate is passed through a bark cork 5 mm. thick which fits easily into the hole in the lead. The detonator should project into the explosive at least 25 mm. The explosive is tamped with dry sand which passes a mesh of 0·35 mm. and weighs about 1·300 g. per litre. This is poured without agitation on to the cork. Tests are carried out to ascertain the charge that produces the same enlargement as 15 g. of picric acid fired under the same conditions. It is not necessary to continue the tests until the exact equivalent has been found as the enlargement V is related to the weight of charge by the formula $V = KC^{1\cdot4}$. The following are the co-efficients thus obtained, picric acid being taken as 100 :

Picric acid	100
Blasting gelatine	155
Dynamite No. 1	102
Grisoutine roche	100
,, couche	75
Grisounaphthalite roche, N_1b	103
,, couche, N_1a	81
,, salpêtrée, N_4	78
Favier N_1c	111
Na Cheddite O. No. 5	86
Cheddite O. No. 2	82
Mining powder, strong	52
,, ,, ordinary	48

Black powder, or other non-detonating explosive, is mixed first with a suitable high explosive.

The Trauzl test in trials at D'Anzin in 1897 gave results in good agreement with those obtained in the mine : [2]

Explosive	Theoretical Potential Q	Power by Bomb Test	Trauzl Test	Industrial Result
Blasting gelatine	100	100	100	100
Dynamite No. 1	73	67	66	67
Grisoutine (70 per cent.)	41	72	66	69
Grisoutine B Ablon (88 per cent.)	37	60	50	53
Blasting powder (ordinary)	43	28	31	31

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[1] Vennin et Chesneau, p. 101 ; *P. et S.*, vol. 15, p. 227.

[2] Vennin et Chesneau, p. 109.

Kling and Florentin have found that the results are not affected appreciably by reducing the temperature of the explosive to −80° or even to −190°.[1]

Earth test.

Tests are also carried out in France in the earth in a meadow where the soil is as uniform as possible and has not been disturbed for many years.[2] Holes are drilled 2 metres apart, 1 metre deep, and 29 mm. in diameter. These are charged with 150 to 200 g. of the explosive and fired with No. 7 detonators. There should be no projection of earth. The diameter D and the height H of the cavity formed are measured and the capacity is calculated from the formula $V = \frac{1}{6} \pi D^2H$. From this the volume of the original drill hole is deducted and the difference is the measure of the power of the explosive. The tests are carried out in comparison with a standard explosive of the same type. The results do not always place the explosives in the same order as the Trauzl test or as trials carried out in mines under actual working conditions, as is shown by the following figures obtained at D'Euville in 1910:

Explosive	Power by Bomb Test	Earth Test	Trauzl Test	Industrial Result
Picric acid	100	100	100	100
Favier N_1c	90	102	104	111
Cheddite O_2	67	115	86	90

Concrete test.

Blocks of concrete 500 mm. in diameter and height are also used sometimes with charges of 5 to 10 g. of explosive. The results obtained are much the same as those yielded by the Trauzl test, but are not so readily expressed in figures.[3]

Ballistic pendulum.

Another appliance, that is used to determine the comparative strength of explosives, is the ballistic pendulum. The Inspector of Explosives adopted it in England in 1900 in place of the Trauzl lead block for testing the strength of explosives for use in coal-mines. It is used for the same purpose by the U.S. Bureau of Mines, although they also carry out tests with the lead block, which is generally used on the Continent. The test consists in firing a stemmed shot from a steel gun into a heavy mortar, which is suspended from a bearing. The swing imparted to this pendulum is a measure of the power of the explosive. The pendulum at the Rotherham Testing Station consists of a 13-inch mortar weighing 5 tons 1 cwt., suspended at a distance of 92 inches from a roller bearing. A charge of 4 oz. of the explosive is loaded into a gun, such as was used in the Woolwich test for permitted explosives, and tamped in a

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[1] *P. et S.*, vol. xvii., 1913, p. 151

[2] Vennin et Chesneau, p. 104; *P. et S*, vol. XV., p. 229.

[3] Vennin et Chesneau, p. 105.

standard manner. The gun is wheeled up until a distance of exactly 2 inches separates it from the mortar and is fired electrically with a detonator of the strength recommended by the makers of the explosive. The swing is measured, and is compared with that given by 4 oz. of 60 per cent. gelignite under the same conditions. This standard explosive produces a swing of 3·27 inches.

The American Bureau of Mines use a 12·2 inch mortar weighing 14 tons 2 cwt., suspended at a distance of $89\frac{3}{4}$ inches from a knife-edge bearing (*see* Fig. 94). The standard charge is 8 oz. of 40 per cent. American straight dynamite, which is stemmed with 1 lb. of dry clay. The gun is brought up to a distance of $\frac{1}{16}$ inch from the mortar and fired electrically. The standard explosive produces a deflection varying between 2·7 and 3·1 inches, the result being affected by the wind, the exact position of the knife-edges, and other causes. Some charges of the standard explosive are fired on every day that tests are carried out to establish the "unit swing" for the day. Charges of the explosive under test are then fired until it is ascertained what will give

Fig. 94. Ballistic Pendulum (from *Bureau of Mines Bulletin*, No. 15)

about the same swing. Three of these charges are then fired, and from the mean the charge that would produce exactly the unit swing is calculated by simple proportion.

The momentum acquired by the pendulum is equal to $2\ W\ \sin\frac{a}{2}\times\sqrt{\frac{r}{g}}$, where W is the weight of the pendulum, a the angle through which it is deflected from the vertical, r its radius, and g the acceleration due to gravity. For small deflections we may write $2\ \sin\ \frac{a}{2}=\frac{s}{r}$, where s is the linear deflection of the centre of gravity of the pendulum from the vertical. Hence the momentum is $\frac{W\,s}{\sqrt{g\,r}}$, and as W, r and g are all constant the momentum is proportional to s. If the stemming and all the products of explosion were brought to rest within the mortar, their momentum would be equal to that imparted to the mortar. But the gaseous products and part of the solids are blown out again and so must impart more momentum.

One of the advantages that led to the adoption of the ballistic pendulum in place of the lead block at the Home Office Testing Station is that it gives a truer measure of the relative strengths of detonating and non-detonating explosives. The swing given by 4 oz. of dynamite was found to be 2·3 times as great as that given by the same quantity of black powder, whereas the average of the estimates given by seventy-two practical miners was 2·29.[1] The ratio given by Bichel's measurements of the pressure (*see* above) is $48{\cdot}2/18{\cdot}7 = 2{\cdot}58$.

In 1906 a large number of practical comparative trials were carried out in coal-mines with four different explosives in connexion with the Bobbinite inquiry, and it was found that the quantities of coal got were in very close agreement with the results that had been obtained with the ballistic pendulum:[2]

Explosive	Coal-getting trials	Ballistic pendulum
Bobbinite	100	100
Carbonite . . .	177	159
Saxonite	257	246
Ammonite	273	261

There is a modification of this test in use, in which the explosive is fired from a suspended mortar, which has a bore that is several inches in diameter near the muzzle, but is contracted further in. The charge is placed in the narrow portion, and over it is placed a round or cylindrical shot, which fills the wide part of the bore. On firing, the mortar recoils a distance, which is

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[1] See *A.R.*, 1900, p. 129.

[2] *A.R.*, 1906, p. 108.

taken as a measure of the power. Comey and Holmes have found that the results are much more uniform, if before each test two shots are fired with blasting gelatine so as to clean out the bore of the mortar very thoroughly.[1]

THE TIME FACTOR

These methods of determining the power of explosives all leave out of account one very important factor, the time required for the explosive to develop its maximum pressure. For some purposes this is of the very greatest consequence: in the case of detonators, for instance, the violence of the blow is of more importance than the total quantity of energy liberated: and for hasty military demolitions, where it is not possible to tamp the charge properly, a very rapidly detonating explosive is also required. On the other hand, for blasting comparatively soft material such as coal, which must not be broken up too much, the explosive should not be too violent.

It has been proposed by Bichel[2] to use the expression $\frac{m v^2}{2}$ for the "brisance" or violence of the blow given by an explosion, m being the mass of gas evolved and v the velocity of detonation. But practical tests do not confirm the idea that the effect is proportional to the square of the velocity of detonation: simple proportionality agrees with the facts better. Moreover, the above expression represents a quantity of energy, that is to say, it has the same dimensions as the indications of the pressure gauge, the lead block and the ballistic pendulum, but what we are now seeking is the intensity of action of an explosive when detonated unconfined. Experiments upon the crushing of small lead cylinders indicate that this can be represented approximately by an expression $KfU\Delta$, where f is the specific pressure of the explosive, U is the velocity of detonation, Δ is the density of the explosive, and K is a constant.[3] The matter is, however, complicated by the fact that the brisance of a cartridge is different in different directions: if a cylindrical cartridge be detonated from one end, the action in the direction in which the detonation proceeds is considerably greater than in the opposite direction. Thus Kast found that a charge of trinitro-toluene detonated in an upright position over a lead cylinder reduced its length 2·81 mm. when the detonator was at the top, and only 1·73 mm. when it was at the bottom of the cartridge. Taffanel and Dautriche have also shown that there is a great difference in the shock produced from the two ends of a cartridge,[4] as revealed by the far greater distance at which a second cartridge can be detonated by influence, according to relative position:

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[1] *8th Int. Cong. Appl. Chem.*, 1912, vol. xxv., p. 209.

[2] *S.S.*, 1908, p. 343.

[3] *See also* Kast, *S.S.*, 1913, p. 65

[4] *Compt. rend.*, 153, 1911, p. 823.

Explosive	Direct detonation Second cartridge		Inverse detonation Second cartridge	
	Exploded at cm.	Did not explode at cm.	Exploded at cm.	Did not explode at cm.
Grisoutine . . .	30	40	10	20
Grisoulite-roche . .	5	8	—	1
Grisoulite-couche salpétrée	5	8	1	2
Carbite d'Ablon . .	12	16	1	2

Soon after the invention of the first high explosives it was realized that the detonation was propagated as a wave, similar to a wave of sound, and measurements of the velocity were carried out by Abel, Berthelot, and others. The method adopted consisted in detonating a long string of cartridges, near the two ends of which wires were passed through the explosive. These were connected to the two circuits of a Boulengé or other chronograph, and so a record was obtained of the time that was required for the detonation to travel between the two points selected. But as these chronographs only give readings to a few 10,000ths of a second, and in this time the detonation travels a metre or more, it was necessary to make the train 35 or more metres long to obtain an accurate result.

Mettegang recorder.

A better method was devised by Mettegang, who adapted the idea of Noble's chronoscope.[1] The record is obtained by means of induction sparks on a smoked drum, which is rotated rapidly by means of an electric motor. The drum is provided with a speed recorder and a device for measuring small distances on it. The latter consists of a microscope with spider line for observing the surface of the drum, which is moved round by an endless screw fitted with a dial. Each complete rotation of the screw corresponds to 1 mm. on the surface of the drum. It is rotated until one of the spots made by an induction spark comes under the spider line of the microscope. On the dial the position can then be read to 0·01 mm. The position of the spot made by one of the other induction circuits can then be ascertained in the same way. As the drum can be rotated by the electric motor with a peripheral velocity of 100 metres per second, readings can be obtained to one 10,000,000th part of a second. It is possible with this to measure the velocity accurately with a string of cartridges 1 metre long, or even half this, and obtain an approximate estimate with considerably shorter trains. The apparatus is arranged for six different induction circuits. The primary circuits pass through wires

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[1] *Trans. Roy. Inst.*, 1871.

crossing the train of explosive at different points, and are supplied with current from an accumulator. When this current is interrupted by the breaking of the wire, a current is induced in the corresponding secondary circuit, one wire of which is in permanent contact with the drum, and the other terminates in a platinum point, which is brought quite near to its surface.[1]

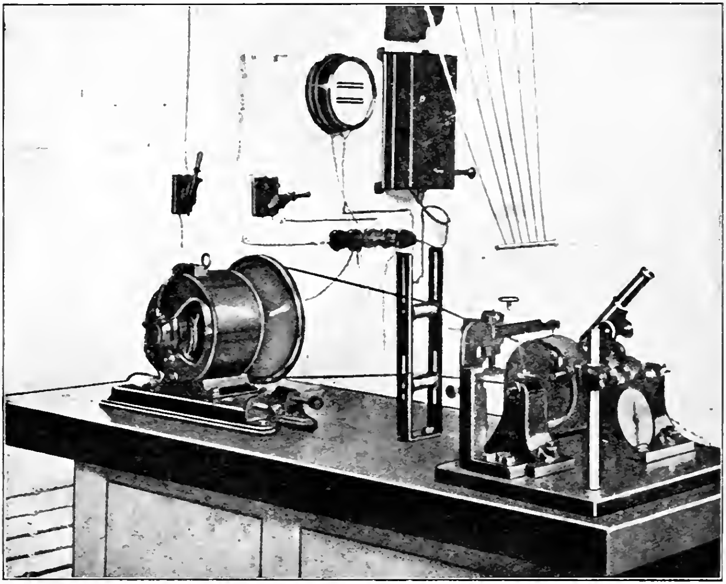

FIG. 95. Mettegang Time Recorder for Determining the Velocity of Detonation

The sources of error of an apparatus of this type have been examined by Kast.[2] The wire passing through the explosive should be as thin as possible; Kast used copper wires 0·1 mm. thick. They should be fastened as firmly as possible. When the explosive was detonated in metal tubes Kast passed the wires through little vulcanite plugs in the walls, pulled them tight and

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[1] For further descriptions *see* Mettegang, *Report of 5th Cong. Appl. Chem.*, vol. ii., p. 327; *Gluckauf*, 1904, p. 1046; Kast, *Spreng- und Zündstoffe*, p. 1025; Bichel, *Testing Explosives*, Chapter V; *S.S.*, 1908, p. 403; Hall, *U.S. Bureau of Mines Bulletin* 15, p. 92.

[2] *S.S.*, 1913, p. 91.

wound them on to the outside of the plugs before joining them to the connecting wires. Similarly when the explosive was detonated without envelope, it was laid in a wooden trough and the thin wires were fastened firmly to nails, and made to pass either through the explosive, when it was soft, or over its surface in the case of such substances as cast picric acid. The distance of the platinum points from the surface of the drum should only be about 0·1 mm., to avoid danger of the spark springing to one side. The different circuits should, of course, be as similar as possible one to another. The currents should be equal and steady, and should proceed in the same direction in all cases. The mark on the drum is never made at the same instant as the detonation wave reaches the wire: there is always a delay due to various causes, which although short in actual duration, is long compared with the sensitiveness of the instrument. Hence the great necessity to have the causes of delay equal in all the circuits. In order to diminish the self-induction in the circuits, which is one of the causes of delay, the iron cores of the induction coils have been done away with at the American Testing Station.

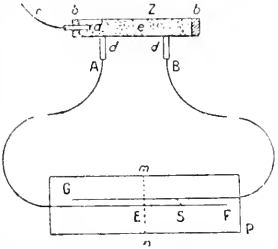

Fig. 96. Dautriche's Method for determining the Velocity of Detonation

Dautriche's method.

A very simple and ingenious method of measuring the velocity of detonation has been devised by Dautriche.[1] It is based upon the use of detonating fuse, the rate of detonation of which is very uniform and is determined by the manufacturers, MM. Davey, Bickford, Smith et Cie., by the method described above. The arrangement of the test is shown in Fig. 96. The explosive is compressed into the tube z to a known density, and into one end a detonator d is inserted. Two other detonators are inserted into the sides of the tube at a distance from one another of 100 mm., or other selected interval, and into these are inserted the ends of two pieces of detonating fuse, AF and BG 1000 and 800 mm. long respectively. The other ends of these pieces of fuse lie alongside one another on a slab of lead P for a distance of about 200 mm. The mid-point E between F and G is marked on the surface of the lead. When the explosive is detonated by means of the first detonator, the detonation communicated to the two pieces of fuse, and the point where the two waves of detonation meet is shown by a sharp line S, which is formed on the surface of the lead. The distance ES is measured, and the velocity of detonation can then be calculated from the formula.

$$V = U \times \frac{AB}{200 + 2 \times ES}$$

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[1] *Compt. rend.*, 143, 1906, p. 641.

where U is the known velocity of detonation of the fuse, and V is the velocity of detonation of the explosive under examination. More often now only one piece of fuse is used, both ends of which are inserted into detonators at different points in the cartridge of explosive. The middle part of the fuse is firmly attached to the slab of lead, and the centre point M of the fuse is marked. We then have

$$V = U \times \frac{AB}{2 \times MS}$$

By this method the velocity of detonation can be determined on a single cartridge of the explosive. This is a doubtful advantage, when it is desired to ascertain the intrinsic velocity of the material, as there are great fluctuations in the first part of the charge, but it is of great advantage in ascertaining the actual time that a mining charge takes to detonate.

Velocity of sound.

The velocity of the wave of detonation is of the same order as the velocity of sound waves through solids. This velocity may be calculated from the equation

$$v = \sqrt{\frac{\mu}{d}}$$

where μ is the modulus of elasticity and d is the density. In gases moderate increases of pressure raise the values of μ and d proportionally and consequently do not affect the velocity of sound, but high pressures raise it somewhat. Thus A. W. Witkowski found an increase of 5·7 per cent. in the velocity in air subjected to a pressure of 100 atmospheres.[1] The velocity also increases proportionally to the square root of the absolute temperature, the pressure remaining constant. In liquids the compressibility falls with increase of pressure and rises with increase of temperature. As the modulus of elasticity is inversely proportional to the compressibility, and the density of the liquid is comparatively little affected, the velocity of sound must increase with rise of pressure and diminish with temperature. The modulus of liquids is so very much higher than that of gases that the velocity of sound in the former is several times as great as it is in air in spite of the higher density. In solids the velocity is generally greater than in liquids, but depends upon the properties of the solid.

The wave of detonation must be propagated through the explosive in much the same way as a wave of sound, but the velocity is modified considerably by the enormous pressures generated. When the impulse is very great the wave assumes a form resembling that of a breaker.[2] The theory has been

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[1] *Bull. Acad. Sci. Cracow*, 1899, p. 138.

[2] For a discussion of the propagation of discontinuities through gases *see* M. Vieille *P. et S.*, vol. X., pp. 177–260.

Substance	State	Temperature °C.	Velocity of Sound Metres per sec.
Air	gas	15	340
Hydrogen	,,	0	1270
Water	liquid	15	1437
Ethyl alcohol, 95 per cent.	,,	12·5	1241
Ether	,,	15	1032
Chloroform	,,	15	983
Aluminium	solid	—	5104
Lead	,,	15–20	1227
Iron	,,	15–20	5124
Glass	,,	—	5060
Oak wood	,,	—	3381
Cork	,,	—	500 about
Paraffin	,,	15–17	1304
Tallow	,,	15–17	390
Indiarubber	,,	0	54

advanced by Jouguet and Crussard,[1] amongst others, that the velocity of an explosive wave is the same as the velocity of sound in the medium immediately behind the front of the wave, that is, in the highly heated and compressed gases formed by the explosion. Taffanel and Dautriche [2] have applied this theory to the study of the propagation of the explosive wave in solid explosives and have deduced from it some important formulae, one of which is

$$U = 6{\cdot}41 \frac{\sqrt{f}}{1 - \alpha\Delta}$$

In which U is the velocity of the wave, Δ is the density, α is the co-volume of the products of explosion, and f is the theoretical "force" of the explosive and is identical with pv in the equation at the commencement of this chapter. The velocities found by actual experiment do not agree with those calculated using the ordinary values of f. Hence it is concluded that the chemical changes taking place in the front of the wave are different from those assumed in the calculation of f, and that further changes take place behind the wave. The "explosive pressure" or pressure of the wave is given by the equations

$$p = \frac{2f\Delta}{1 - \alpha\Delta} = \frac{\Delta(1 - \alpha\Delta)U^2}{10{\cdot}8}$$

It is to be remarked that in the first formula the value of p is double the ordinary static pressure developed by the explosive.[3] The explosive pressure

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[1] *Compt. rend.*, 1907, vol. 144, pp. 415, 560; 1913, vol. 157, p. 545.

[2] *Compt. rend.*, 1912, vol. 155, p. 1221.

[3] These equations have been taken from Vennin et Chesneau, p. 90, but there appears to be an error in the numerical factors.

is intimately connected with the brisance of explosives discussed later in this chapter.

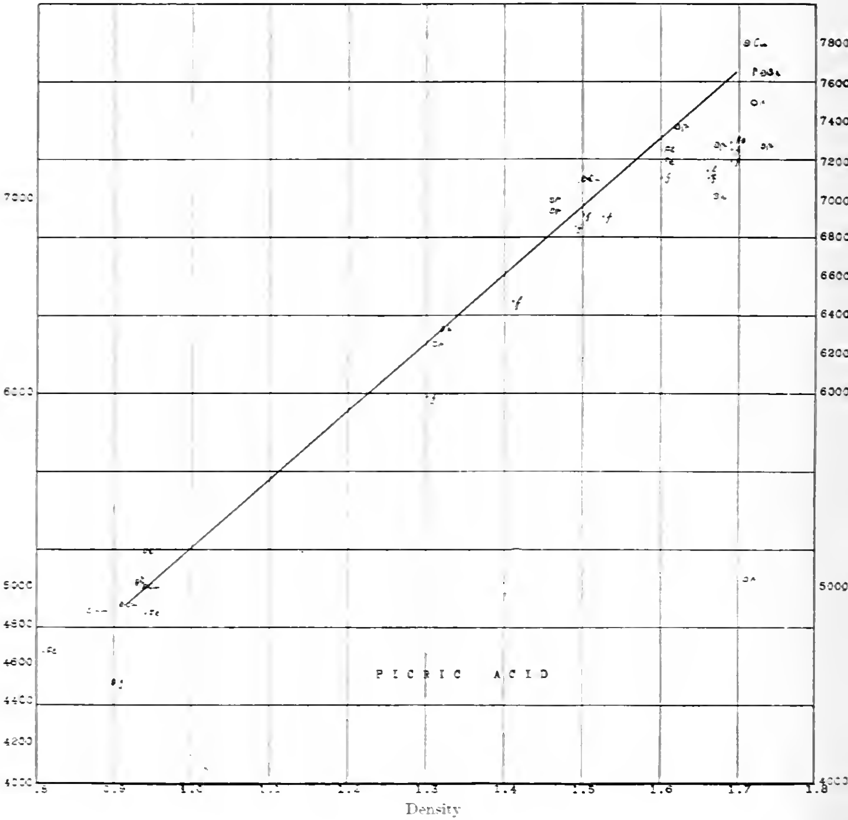

Fig. 97. Velocities of Detonation of Picric Acid

Influence of density.

With increase of density the velocity of detonation of an explosive generally increases. This no doubt is due to diminution of the compressibility and consequent increase in μ, and also to the greater pressure generated. At the same time the sensitiveness decreases, perhaps because the energy imparted to a particle is dissipated more rapidly in the denser and more rigid material, and consequently a more powerful impulse is required to bring the explosive to the point of detonation.

The variation of the velocity of detonation with density in the case of cheddite containing ammonium perchlorate was shown in Fig. 78. Very similar curves have been obtained with other Cheddites, but the fall in the velocity, when the critical density is passed, is apparently due entirely to the insensitiveness of the dense explosive, which renders it impossible to detonate it completely. If complete detonation could be obtained, the velocity would probably continue to rise up to the highest attainable density. Figs. 97, 98, 99 show the effect of variations of density on the velocity of detonation of picric acid, trinitro-toluene and trinitro-benzene based on the determinations of Dautriche[1] and Kast.[2] Both authors have drawn curves to represent their results, but an examination of the data leads only to the conclusion that their results are equally well represented by a straight line.

Influence of diameter.

Other causes which increase the pressure also produce an increase in the velocity of detonation up to a limit. Thus, if the diameter of the column of explosive is too small, there is a diminution in the velocity, but with unmixed nitro-derivatives a diameter of 10 mm. is sufficient to obtain the maximum value. Kast obtained the following results with cast trinitro-toluene of density 1·59 in iron tubes fired with a 1 g. detonator and a priming of compressed picric acid (density 1·58):

Diameter of explosive mm.	Velocity of detonation M/sec.
21	6700, 6555
29	6700
75	6595 mean of 3 experiments
160	6690
220	6675
300	6710
Mean	6649

But with some insensitive explosives the influence extends to somewhat larger diameters. With ammonium nitrate explosives fired by means of 2 g. detonators in iron tubes the following results were obtained:

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[1] *P. et S.*, vol. xvi, p. 27, observations marked ⊙.

[2] *S.S.* 1913, pp. 65, 88, 133, 155 and 172, marked ·.

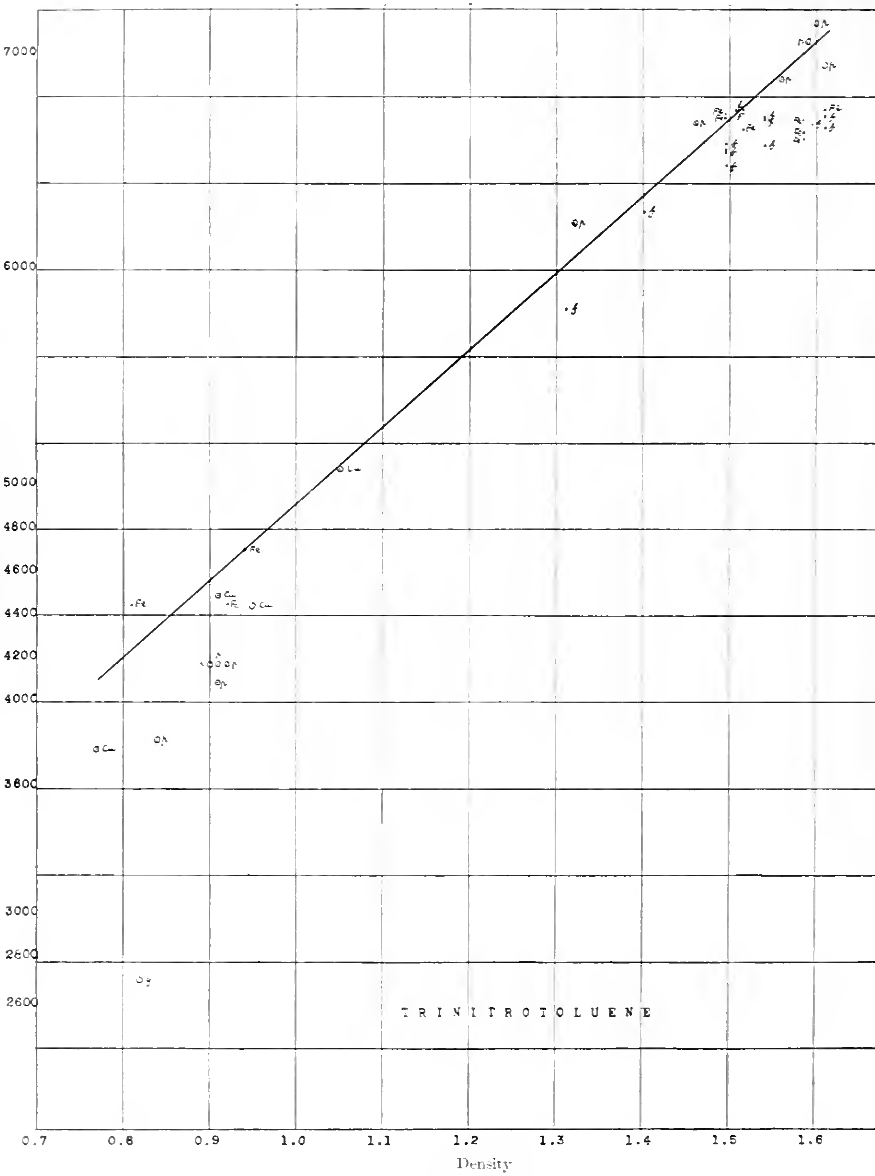

Fig. 98. Velocities of Detonation of Trinitro-toluene

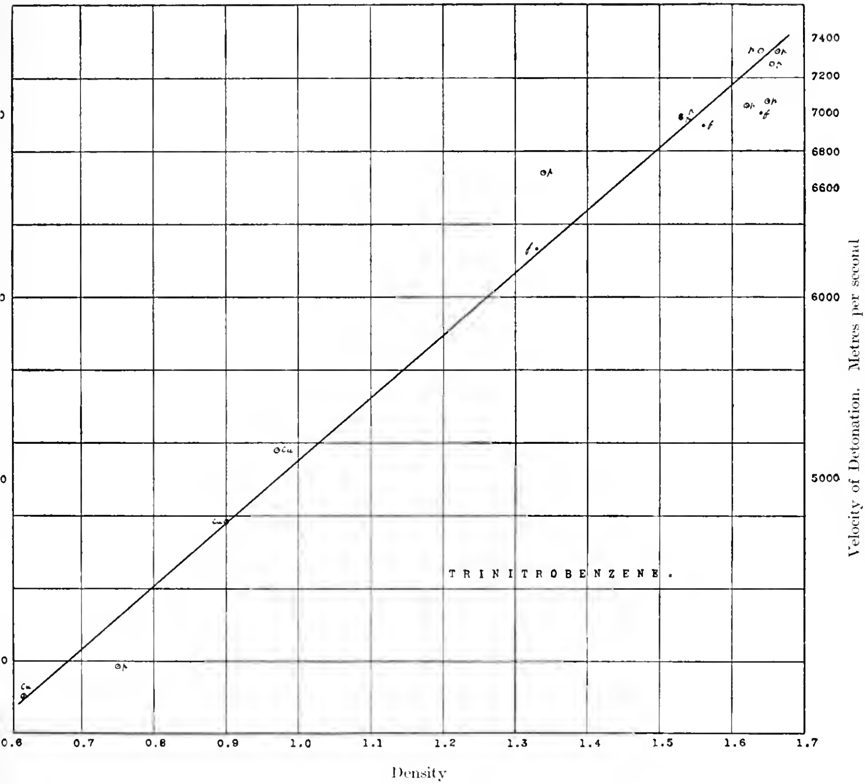

Fig. 99. Velocities of Detonation of Trinitro-benzene

Influence of envelope.

On Figs. 97, 98, 99 are marked the nature of the envelopes surrounding the columns of picric acid, trinitro-toluene and trinitro-benzene, when they were detonated. *Fe* means iron tube, *Cu* copper tube, *p* paper, *g* glass, and *f* free. It will be seen that with these explosives the velocity of detonation was not much affected by the strength of confinement. With ammonium

Explosive			Density	Velocity of detonation in tubes of diameter		
				26 mm.	40 mm.	50 mm.
Aldorfit . .	Ammon. nitrate	81	1·10	—	4825	—
	Trinitro-toluene	17	1·14	4410	—	—
	Rye meal	2	1·15	4430	—	—
			1·16	—	4925	—
			1·17	—	—	4960
Gesteinsdorfit .	Ammon. nitrate	66	1·10	3940	—	—
	Potas. nitrate	5	1·11	—	4420	—
	Trinitro-toluene	15	1·15	4045	4505	—
	Sod. chloride	10	1·17	—	—	4605
	Rye meal	4	—	—	—	—

nitrate explosives the effect is much greater, thus Bichel has recorded the following results:

Explosive	Velocity of detonation	
	Unconfined	Confined
Donarite	3930	4137
Ammon-carbonite I	1753	3195
Ammon-carbonite	1649	3094
Thunderite	2137	3654

Influence of primer.

The strength of the detonator or priming has but little ultimate influence, provided that it be strong enough to start the wave of detonation, but at the commencement of the train there are often great irregularities: the velocities there may be either high or low, according to the strength of the igniter. Thus with cast trinitro-toluene, specific gravity 1·60, in iron tubes Kast obtained the following results in different parts of the columns:

Priming	Velocity of detonation measured over the distance			
	100–200 mm.	200–405 mm.	405–505 mm.	
65 g. picric acid (1·58) .	3910	6415	5710	
950 g. trinitro-toluene (1·54)	10580	6880	5080	
	10–160 mm.	160–310 mm.	310–460 mm.	460–1060 mm.
21 g. picric acid (1·58) .	5420	5795	6330	6590
600 g. trinitro-toluene (1·45)	7520	6000	6680	6590

The velocities measured over very short distances are not very accurate, but the above figures are in all cases the means of three different experiments yielding similar results. With moderate ignition the results are fairly uniform, and is shown by the following velocities recorded on the section 340 mm. to about 1060 mm. with trinitro-toluene (specific gravity 1·53 to 1·54):

0·65 g. detonator	missfires
0·8 g. ,,	6570
1·0 g. ,,	6650
1·5 g. ,,	6540
2 g. ,,	6570
3 g. ,,	6560
1 g. detonator and 10 g. picric acid (1·58)	6800

When the velocity has attained its proper value, it remains constant over an indefinite length:

Section	Picric acid 1·60 1 g. detonator	Trinitro-toluene 1·52 1 g. detonator and 10 g. picric acid
20–1020 mm.	7100	6740
1020–2020 mm.	7154	
2020–3020 mm.	7054	6630
3020–4020 mm.	7100	6710
4020–5020 mm.	7010	6755

The more insensitive explosives are, however, incapable of maintaining the velocity of detonation. Thus Monachit, consisting of 81 per cent. ammonium nitrate, 13 per cent. liquid nitro-derivatives, 5 per cent. saltpetre and 1 per cent. flour, gave:

Density	Velocity of detonation in section			Ignition
	150–250 mm.	250–630 mm.	630–730 mm.	
1·02	4885	4440	3345	2 g. detonator
1·35	4230	3495	3135	2 g. detonator and 140 g. T.n.t.
1·56	4745	1730	1270	2 g. detonator and 127 g. T.n.t.

Even explosives such as picric acid show signs of behaving in the same way at the highest densities, whether they be cast or compressed.

The temperature of the explosive has little or no influence on the velocity

Effect of temperature.

of detonation, although it affects the sensitiveness considerably. The following results were obtained by A. Kling and D. Florentin:[1]

	Density	Velocity of Detonation Ordinary temperature	 About $-190°$
Fulminate	1·25	2250	2350
Cheddite No. 2	1·00	2365	2080
Picric acid	1·01	4470	4750

The velocities were determined by Dautriche's method: to ensure detonation the explosive in the neighbourhood of the detonator was not cooled.

Nitro-glycerine.

The behaviour of liquid trinitro-glycerine is curious. The earlier determinations of its velocity of detonation gave very discordant results, and the matter was reinvestigated by Comey.[2] In a tube 6 mm. in diameter detonation from a 1·6 g. detonator was only propagated a few inches. With a 9 mm. glass tube an average velocity of 654 metres per second was obtained, three tests being made with only comparatively small variations from the average. With 25 mm. iron tubes five tests were made, which fell into two groups, the results being 1539 and 1463, mean 1501 metres per second, and 6783, 7877 and 8410, mean 7690. In a 38 mm. iron pipe with a 1·6 g. detonator the velocity was 8527 metres per second, but with a 0·8 g. detonator the results were 1288, 2412 and 1627. Using a detonating fuse as primer, four closely concordant results were obtained averaging 7234 metres per second. Thus, two widely differing velocities were recorded with no intermediate values. Apparently under a moderate blow the elasticity of nitro-glycerine is that of a liquid, but under a very violent impulse it behaves like a solid. The velocity of sound in water is about 1440 metres per second at 13° and 1530 at 30°. Blochmann[3] gives the value 1525 metres per second for both di- and trinitro-glycerine.

Nitro-glycerine explosives.

Comey also determined the velocities of detonation of a large number of American dynamites of various grades, and the results are given in Fig. 100. For the composition of these explosives *see* Chapter XXV. In the case of the "straight dynamites" the velocity increases steadily with the percentage of nitro-glycerine, and is not affected by variations in the strength of the detonators, nor by the use of primers. The gelatine dynamites differ from these in that the nitro-glycerine is gelatinized with a small proportion of nitro-cotton. When fired with detonators of various strengths, they detonate with a fairly uniform velocity of about 2270 metres per second irrespective of the percentage of nitro-glycerine. But if a primer of 40 per cent. straight dynamite be employed, the velocity is greatly increased, and a curve is obtained almost parallel to that of the straight dynamites, but higher. In the ammonia

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[1] *P. et S.*, vol. xvii., 1913, p. 154.

[2] *Seventh Inter. Cong.*, 1909, IIIb, p. 30.

[3] *Bergbau*, 1905; *S.S.*, 1906, p. 80.

dynamites a large part of the nitro-glycerine has been replaced with ammonium nitrate; the velocity rises to a maximum with the 50 per cent. brand and then falls again. These results were not materially affected by the use of a primer.

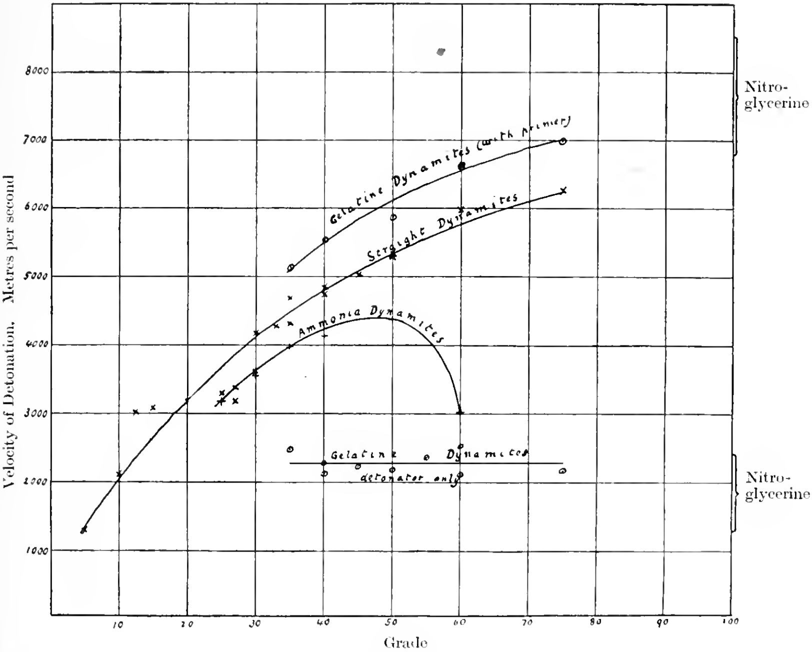

FIG. 100. Velocities of Detonation of American Dynamites

It is seen, therefore, that the gelatine dynamites, which are similar to the gelignites made in Europe, resemble nitro-glycerine itself in having two very different rates of detonation. Comey does not state the densities of the explosives. It was found by C. Herlin that a gelatinized explosive which had a velocity of detonation of 7000 metres per second when new gave only 3000 when a month old and 2000 when a year old.[1]

The following Table gives the velocity of detonation of some other explosives:

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[1] *S.S.*, 1914, p. 401.

Explosive		Diameter mm.	Density	Velocity of detonation m./sec.	Authority
Mercury fulminate	. $Hg(OCN)_2$ . .	6·45	—	3920	Bichel
Mercury fulminate, ordinary temperature .		—	1·25	2474	Kling and Florentin
,, ,, ,, ,, .		—	1·18	2026	
,, ,, at —190° . . .		—	1·25	2310–2411	
Austrian detonating fuse (old pattern) containing mercury fulminate, water and glycerine .		—	—	3000–3500	—
		—	—	4000–5000	Gen. Hess
Austrian detonating fuse M 03	Hg. fulminate 80	—	—	5000–6000	Gen. Hess
	Paraffin 20	—	—	—	—
French detonating fuse (old pattern)	Picric acid powdered in tin tube	—	—	7000	—
(new pattern) .	. T n t cast in lead tube	—	—	6000–6500	—
		4·3–4·5	1·5	4800–4990	Bichel
				6880	Dautriche
Italian detonating fuse	Ballistite and Black powder	5·5	—	5000	—
Gun-cotton		2	·69–·73	3700–3800	Berthelot
		<4	·9	3900	,,
		2	1·17	4800	,,
		<4	1·2	4300	,,
		3·1	1·27	5400	,,
		<4	1·4	4800–6200	,,
		—	1·25	6380	Bichel
		23	·82	5220	Abel
Gun-cotton, wet .	. 15 per cent. water .	23	—	5540	,,
	30 per cent. water .	23	—	5830	,,
	,, ,,	31	—	5230	Bichel
Nitro-hydro-cellulose		4	—	4900	
		5·5	—	6100	
Nitro-starch.		4	1·1–1·2	5000	Abel
		4	1·35	5500	Berthelot
Nitro-mannite		4	1·5	6900–7100	
		4	1·9	7700	
Tetranitro-methylaniline		—	—	8455	Bichel
		21	1·53	7075–7215	Kast
		21	1·57	7155	,,
		21	1·63	7215	,,
Trinitro-chlorbenzene (compressed). . .		21	1·70–1·71	6855	,,
		21	1·72–1·73	6960	,,
		21	1·74–1·75	7130	,,
,, ,, (cast)		29	1·76	7150	,,
Hexanitro-diphenylamine		21	1·58	7100	,,
		21	1·67	7150	,,

Explosive			Diameter mm.	Density	Velocity of detonation m./sec.	Authority
Trinitro-cresol			21	1·52	6620	Kast.
			21	1·54	6400	,,
			21	1·62	6850	,,
Dinitro-benzene (confined)			21	1·4	6160(?)	,,
			21	1·5	6000	,,
Methyl nitrate			3	1·18	2100	Berthelot
Panclastite	$CS_2 + N_2O_4$		3	1·35	4600–6600	,,
NITRO-GLYCERINE EXPLOSIVES						
Dynamite No. 1	N/G	75	3	—	2300–2800	Berthelot
	Guhr	25	6	—	1900–3200	,,
			30	1·58	6820	Bichel
			20	·63	1990	Dautriche
			20	·79	2400	,,
			20	·85	2560	,,
			20	1·34	3670	,,
			20	1·54	5230	,,
			20	1·62	6800	,,
			20	1·69	4200	,,
			20	1·71	2460	,,
			20	1·74	failed	,,
			—	1·39	6370	Kast
			26	1·43	2680–6040	,,
			24	1·65	6300	Dautriche
Blasting gelatine	N/G	92–3	30	1·63	7700	Bichel
	Col. Cot.	7–8	—	1·58	1535	Kast
			—	—	1800–4000	Mann
Gelatine dynamite	N/G	62–63·5	30	1·67	7000	Bichel
	Col. cot.	1·5–3	—	1·59	2055	Kast
	$NaNO_3$	27	—	—	—	—
	Wood-meal	8				
Gelatine dynamite, British formula			—	—	1910–2521	Mann
Gelignite, British formula			—	—	1643–2702	,,
American dynamite 30 per cent			—	—	4548	Hall and Howell
,, ,, 60 ,,			—	—	6246	
Dynamite 50 per cent. No. 3	N/G	50	—	1·56	4610	Kast
	Guhr	7				
	KNO_3	33·1				
	Wood-meal	9·7				
	Chalk	0·2				
Dynamite 40 per cent.	N/G	40	—	1·56	4440	Kast
	$NaNO_3$	42				
	Wood-meal	16·7				
	Chalk	1·2				

Explosive			Diameter mm.	Density	Velocity of detonation m. sec.	Authority
Extra-Carbonite	N. G.	35	—	1·13	3970	Kast
	Col. cot.	0·3	—	1·20	4070	,,
	$Ba(NO_3)_2$	4				
	KNO_3	25·5				
	Tan meal	34·8				
	Soda	0·5				
Carbonite II.	N. G.	30	—	1·05	3720	Kast
	$NaNO_3$	24·5	—	1·10	3850	,,
	Flour	40·5	30	1·49	2470	Bichel
	$K_2Cr_2O_7$	5				
Nobel's Wetter-dynamite I.	N. G.	30	—	1·16	3860–3930	Kast
	$NaNO_3$	31				
	Flour	30				
	Wood-meal	6				
	Naphhalene	2				
	Alum	1				
Nobel's Wetter-dynamite II.	N. G.	25	—	1·18	3350	Kast
	$NaNO_3$	32	—	1·25	3750	,,
	Flour	34				
	Wood-meal	3				
	Veg. oil	1				
	Alum	5				
Kohlen-Carbonite	N. G.	25	—	1·16	3160	Kast
	KNO_3	34	30	1·42	2700	Bichel
	$Ba(NO_3)_2$	1				
	Flour	38·5				
	Tan meal	1				
	Soda	0·5				
Carbonite I.	N. G.	25	30	1·55	3042	Bichel
	$NaNO_3$	30·5				
	Flour	39·5				
	$K_2Cr_2O_7$	5				
Carbonite	N. G.	25	30	1·08	2440	Bichel
	KNO_3	30·5				
	$Ba(NO_3)_2$	4				
	Wood-meal	40				
	Soda	0·5				
AMMONIUM NITRATE EXPLOSIVES CONTAINING NITRO-GLYCERINE						
Gelatine Carbonite	N. G.	25·3	30	—	2300	Bichel
	Col. cot.	0·7				
	NH_4NO_3	41·5				
	Glyc. gel.	6·9				
	$NaCl$	25·6				
Donarite	N. G.	3·8	26	0·89	3700[1]	Kast
	Col. cot.	0·2	26	0·9	3770[2]	,,
	NH_4NO_3	80	30	1·31	4140[1]	Bichel
	T. n. t.	12	30	1·31	3930[2]	,,
	Flour	4				

[1] In iron tube.

[2] Unconfined.

Explosive			Diameter mm.	Density	Velocity of detonation m./sec.	Authority
Donarite with Am. oxalate	Donarite	85	26	1·01	4100–4240	Kast
	Am. ox.	15				
Ammon-carbonite	N. G.	4	40	1·06	3380	Kast
	NH_4NO_3	82	26	1·23	3310	,,
	KNO_3	10	30	1·19	3100	Bichel
	Flour	4	30	1·19	1650 [1]	,,
Ammon-carbonite 1.	N. G.	4	30	1·11	3195	Bichel
	Col. cot.	0·2	30	1·11	1753 [1]	,,
	NH_4NO_3	80·3				
	KNO_3	5				
	Starch	4·5				
	Coal dust	6				
			Ammonium Nitrate Explosives			
Thunderite	NH_4NO_3	92	30	1·07	3650	Bichel
	T. n. t.	4	30	1·07	2137 [1]	,,
	Flour	4				
Dynammon	NH_4NO_3	90	26	1·01	4100–4240	Kast
	Red Charcoal	10				
Dynammon	NH_4NO_3	99·5	—	0·865	3380	Bichel
	Charcoal	4·5				
Westfalite	NH_4NO_3	91	26	0·90	3830	Kast
	KNO_3	4	40	1·01	4350	,,
	Resin	5	26	1·06	failed	,,
Dahmenite A.	NH_4NO_3	90·8	26	1·02	3680	Kast
	$K_2Cr_2O_7$	2·2				
	Naphthalene	6·5				
	Curcuma	0·5				
Permonite	NH_4NO_3	42·5	26	1·05	3690	Kast
	T. n. t.	10	26	1·13	3780	,,
	$KClO_4$	32·5				
	Starch	12				
	Wood-meal	3				
Aluminium explosive	NH_4NO_3	44·9	21	1·68	4850	Kast
	T. n. t.	31				
	Al wool	24·1				
Ammonal	NH_4NO_3	72·0	—	0·90	3450	Bichel
	Aluminium	23·5				
	Charcoal	4·5				
Grisounite N_3	NH_4NO_3	15	—	1·38	3800	Dautriche
	$NaNO_3$	58	—	1·25	3200	,,
	T. n. naphthalene	27				
Grisounite N_1c	NH_4NO_3	87·4	—	compressed	3635	Dautriche
	D. n. naphthalene	12·6	—	powder	4100	,,

---

[1] Unconfined.

Explosive			Diameter mm.	Density	Velocity of detonation m./sec.	Authority
			CHLORATE EXPLOSIVES			
Cheddite 02	KClO	79	—	—	2750	Vennin
	M/n/naphthalene	1				
	D/n/toluene	15				
	Castor oil	5				
	NH_4ClO_4	82	—	0·67	2900	Dautriche
	D/n/toluene	13	—	0·85	3595	,,
	Castor oil	5	—	0·94	3801	,,
				1·04	4020	,,
				1·16	3974	,,
				1·25	3768	,,
			—	1·34	failed	,,
	NH_4ClO_4	50	—	0·72	2655	,,
	$NaNO_3$	30	—	0·94	3124	,,
	D/n/toluene	15	—	1·04	3361	,,
	Castor oil	5	—	1·17	3355	,,
				1·23	3291	,,
				1·34	3006	,,
Cheddite 60bis 01	$KClO_3$	80	12–20	0·70	2100	Dautriche
	M/n/naphthalene	13	12–20	0·80	2248	,,
	D/n/toluene	2	12–20	0·90	2430	,,
	Castor oil	5	12–20	1·00	2504	,,
			12–20	1·10	2550	,,
			12–20	1·20	2510	,,
			12–20	1·30	2360	,,
			12–20	1·38	2166	,,
			40	0·70	2283	,,
			40	0·80	2385	,,
			40	0·90	2608	,,
			40	1·01	2769	,,
			40	1·17	2901	,,
			40	1·29	2846	,,
			40	1·35	2777	,,
			40	1·40	2451	,,
			40	1·50	failed	,,
			GUNPOWDER, ETC.			
Gunpowder	KNO_3	75	30	1.04	200–300	Bichel
	Charcoal	13				
	Sulphur	12				
Blasting powder, FF, American			—	—	469	Hall and Howell
Judson Powder			—	—	1018	

EFFECT OF ADDITIONS ON THE VELOCITY OF DETONATION OF AROMATIC NITRO-EXPLOSIVES (KAST)

Mixture			Conditions	Diameter	Density	Velocity of detonation	Velocity of detonation of principal constituent at same density
Tetranitro-methylaniline Dinitro-benzene		63 37	Compressed Unconfined	21	1·58	6960	7160
T/n/t D/n/t		90 10	Compressed or cast In iron tube	21–29	1·56–1·59	6620	6680
T/n/t D/n/t		50 50	In iron tube Compressed In iron tube Cast	21–29 21–29	1·52 1·52	6220 failed	6660 —
Plastrotyl	T/n/t Resin	99·5 0·5	Pressed into iron tube	26	1·33	5520	5920
Macarite	T/n/t $Pb(NO_3)_2$	30 70	Unconfined	21 21	2·73 2·89	4700 4850	— —
Triplastite	T/n/t D/n/t Col. cot. $Pb(NO_3)_2$	70 1·2 28·8	Pressed into iron tube	26	1·45	5030	6400

In Kast's experiments the nitro-glycerine and ammonium nitrate explosives were always fired with a 2 g. detonator, but the aromatic nitro-explosives were detonated by means of a primer of loosely compressed picric acid or trinitro-toluene. In the case of the nitro-glycerine explosives, the velocity of detonation is seen to be dependent largely on the percentage of nitro-glycerine. But the addition of nitro-glycerine to ammonium nitrate explosives does not seem to affect the velocity of detonation to any great extent. The addition of dinitro-derivatives to the more highly nitrated compounds does not affect the velocity much more than the simple reduction of density would. Lead nitrate, on the other hand, reduces the rate of detonation considerably.

Brisance meter.

There are other simpler tests for ascertaining the comparative brisance of explosives. The one that is most satisfactory is probably that in which the crushing effect on metal cylinders is measured. A test devised by Hess and used in Austria consists in detonating a charge of 100 g. on the top of two lead cylinders supported on a heavy iron base.[1] The shortening of the upper cylinder is taken as a measure of the brisance, whereas that of the lower one is supposed to be affected more by the pressure exerted. In the Prussian Military Research Department the conclusion was arrived at that the results were not always satisfactory, and a different form is used there,

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[1] *See* Guttmann, *Manuf. of Expl.*, vol. ii., p. 357 ; Berger, *S.S.*, 1906, p. 151.

which is shown in Fig. 103.[1] On the steel base *a* there is fitted a hollow steel cylinder *b*, in which moves a well-fitting steel piston *c*. This carries a strong nickel steel plate *d*, 20 mm. thick and weighing 320 g., which is protected above by two round lead discs 4 mm. thick, on which the explosive is detonated, and which are renewed each time. The piston is purposely made heavy so that it may not move appreciably before it has received the full force of the blow. The crushing of the copper cylinder *e* is proportional to the area of the base of the cartridge, but, as has recently been found by Kast, it is only affected by the height of the cartridge up to a limit.[2] Thus with picric acid,

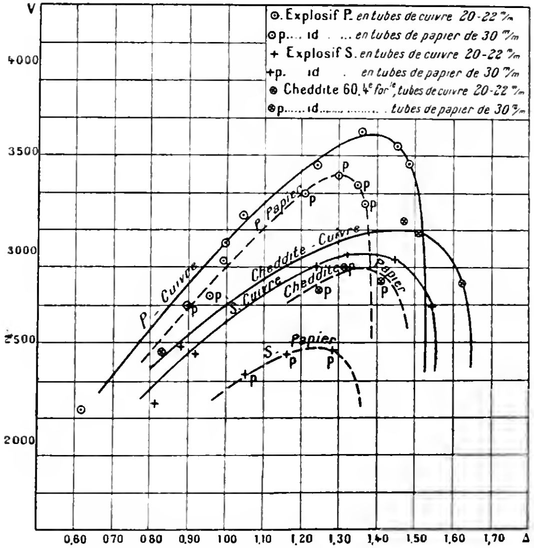

FIG. 101. Velocity of Detonation of Cheddites

Composition	Per 04	S	No. 60
Potassium Chlorate	90	—	80
Sodium Chlorate	—	89	—
Paraffin	10	11	—
Castor Oil	—	—	6
Mononitronaphthalene.	—	—	12
Picric Acid	—	—	2

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[1] Kast, *Spreng- und Zundstoffe*, p. 1031.

[2] *S.S.*, 1913, p. 89.

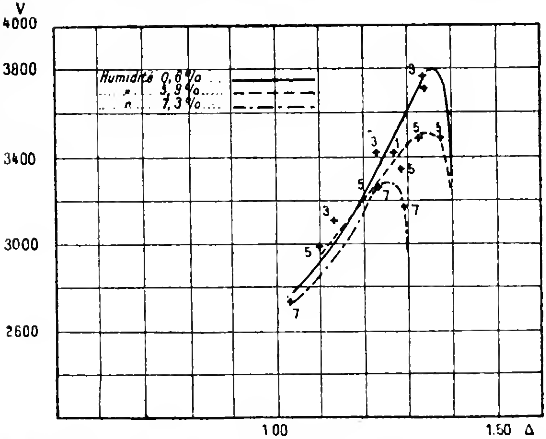
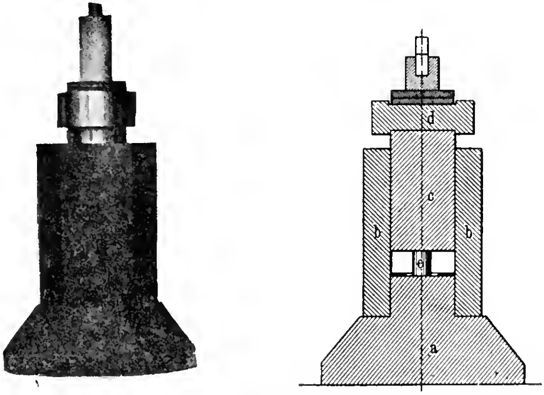


Fig. 102. Effect of Moisture on the Velocity of Detonation of Explosive N3

Sodium Nitrate	58
Trinitronaphthalene	27
Ammonium Nitrate	15



View Section

Fig. 103. Brisance Meter

specific gravity 1·5, compressed into cartridges 21 mm. in diameter but of varying lengths, the following compressions were obtained:

Detonator	Cartridges		Compression mm.
	Weight gr.	Length mm.	
2 g.	15·0	30·8	3·49
„	20	40·9	3·65
„	25	51·2	3·79
„	30	61·5	3·85
„	35	69·3	4·09
„	40	78·0	3·96
3 g.	30	61·4	3·79
„	34·8	71·9	4·02
„	40	80·2	4·04
„	45	90·8	3·81

Similar results were obtained with trinitro-toluene and Macarite.

When the length of the cartridge is not much greater than the diameter, the wave front is curved, and consequently does not all arrive at the bottom end of the cartridge at the same instant; this spreading of the blow over an interval of time apparently causes a weakening of the effect. To obtain comparable results, the cartridges of different explosives should be made up of the same dimensions, or preferably of sufficient length to get the maximum effect. Unfortunately, most of the experiments that had been carried out in the past have been made up with a fixed weight of explosive, 10 or 15 g., and so short that the maximum effect has not been attained. The result is that the relative effect of the denser explosives appears less than it should, as the cartridges are shorter.

It has been suggested above (p. 476) that the brisance is proportional to the product $fU\Delta$, where f is the specific pressure of unit weight of the explosive, and U is the velocity of detonation, and Δ the density. It has also been mentioned that f is proportional to the kinetic energy of the gases of explosion. Unfortunately, the only published tests that have been carried out with sufficiently long cartridges are those by Kast on the three explosives already mentioned:

Explosive	Density Δ	Velocity of Detonation U	Relative Energy f	$\frac{fU\Delta}{10000}$	Compression of Copper
Picric acid . . .	1·5	7000	100	105	4·05
Trinitro-toluene . .	1·5	6600	94	93	3·59
Macarite . . .	2·6	4500	104	122	4·38

The relative potential energy of trinitro-toluene is obtained from the Trauzl tests carried out by Bichel,[1] and that of Macarite from the pamphlet of the inventors, who call it "free spécifique." The relative brisance of the three explosives is as follows, that of picric acid being taken as 100 :

	By calculation $fU\Delta$	By direct measurement Compression of copper
Picric acid	100	100
Trinitro-toluene . . .	89	89
Macarite	116	108

The following table gives the brisance of a number of explosives calculated in the same way :

Explosive.	Density D	Trauzl Test E	Velocity of Detonation U	Brisance $\frac{E.U.D.}{10000}$
Blasting gelatine (with primer) .	1·6	650	7500	780
Gelatine dynamite ,, ,, .	1·6	490	6700	525
Dynamite No. 1	1·58	510	6000	486
Picric acid	1·7	320	7700	420
,, ,, ...	1·6	320	7300	374
Trinitro-toluene	1·6	290	7000	324
Donarite	1·31	487	4100	261
Guncotton	1·12	420	5300	249
Blasting gelatine (without primer) .	1·6	650	2200	210
Mercury fulminate	2·5	213	3920	209
Cheddite 60	1·4	288	3100	125
Kohlen-carbonite	1·42	290	2700	111
Carbonite	1·08	266	2440	70
Gunpowder	1·04	187	280	5

Kast also measured the compression produced by various explosives at different densities using cartridges weighing 15 g. each, 21 mm. in diameter and having a hole for the detonator 15 mm. deep and 9·2 mm. diameter :

[1] *Marine Rundschau*, Nov. 1905.

Explosive	Density	Compression	Velocity of detonation
Tetranitro-methylaniline . .	1·42	3·57	—
	1·53	3·91	7145
	1·59	3·94	7160
Picric acid	1·34	2·81	6160
	1·46	3·34	6700
	1·53	3·55	7000
	1·60	3·88	7100
Trinitro-chlorbenzene . .	1·66	3·36	6800
Hexanitro-diphenylamine .	1·32	3·32	—
Trinitro-benzene	1·35	2·93	6300
	1·51	3·39	6900
	1·60	3·35	7000
Trinitro-cresol	1·37	2·78	—
	1·46	2·99	—
	1·63	3·31	6850
Trinitro-toluene	1·34	2·80	5940
	1·45	2·93	6400
	1·50	3·13	6590
	1·60	3·13	6680
Dinitro-benzene	0·93	1·61	—
Macarite	2·65	2·52	about 4600
	2·75	2·86	4700

In considering the relation between the results of the crusher test and the velocity of detonation, account must be taken of the conditions under which the test is carried out: the explosive is unconfined, and the effect is measured before the velocity has had time to settle down to its steady value. The value of the crusher test lies in the fact that it affords in a simple manner a measure of the practical effect that may be expected when the explosives are used for the hasty demolition of structures for military purposes.

Other tests for brisance.

The brisance of different explosives can also be compared by detonating them on plates or discs of lead or steel and comparing the cavities formed. Unfortunately, this method does not lend itself readily to measurements, but the results are frequently instructive.[1] It is much used for testing detonators, quite small lead plates being used.

For testing explosives for military demolitions soft steel plates are used in France.[2] These measure 500 × 150 × 25 mm. thick, and rest on two supports 400 mm. apart. On the middle of the plate a charge of 100 to 200 g. of high explosive is detonated and afterwards the depth is measured to which the centre has been bent below the ends. This method can be used for testing grenades.

A. v. Huberth proposes to explode the charge immediately under an iron beam mounted so that a graph of its vertical motion is recorded on a drum rotating on a vertical axle.[3] The height of the rise multiplied by the weight of the beam gives the work done by the explosive under these conditions. From the shape of the curve it is proposed to estimate the time during which pressure is exerted on the under surface of the beam, but this time must be much too short to be measured by such an apparatus.

Tests under water.

Explosives for use in submarine mines have been tested under water, advantage being taken of the incompressibility of water, and its consequent power of transmitting the effect of the explosion to a distance. Blochmann devised a dynamometer which registers the pressure as a function of the time[4] similarly to the pressure gauges of Petavel and Bichel. The curve thus obtained (Fig. 104) has two distinct maxima separated by an interval of about 0·05 second when there is 1 metre of water between the explosive and the dynamometer. Bichel also has carried out experiments with this apparatus,[5] and is of opinion that the first maximum is a measure of the percussive force of the explosive, and the second of the gas pressure. The following are his results; the first series was carried out with equal weights, and the second with equal volumes:

Explosive	Density	Charge	Height of 1st maximum	Height of 2nd maximum
Trinitro-toluene	1·55	500 g.	28·0	29·5 mm.
Gun-cotton, dry	1·25	,,	27·5	30·0 mm.
Ammon-carbonite	1·19	,,	17·0	19·3 mm.
Gun-cotton, dry	1·20	450 c.c.	31·5	35·4 mm.
,, 10 per cent. water	1·20	,,	31·0	35·0 mm.
Picric acid	1·44	,,	31·0	30·0 mm.
Trinitro-toluene	1·61	,,	39·9	37·8 mm.

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[1] *See* Bichel, *Testing Explosives*, p. 61; *Marine Rundschau*, Nov. 1905; *A. and E.* 1906, p. 21; also Hess, *Ang.* 1904, p. 553.

[2] Vennin et Chesneau, p. 108.

[3] *S.S.*, 1915, p. 281.

[4] *Marine Rundschau*, 1898, No. 2.

[5] *Marine Rundschau*, Nov. 1905; *A. and E.*, 1906, p. 21.

Cronquist[1] has measured the effect of explosives under water by the action on hollow lead cylinders placed some distance away. These have a central hole, which is closed by means of a brass plug: the specific gravity is determined before and after, and from the difference the pressure is calculated.

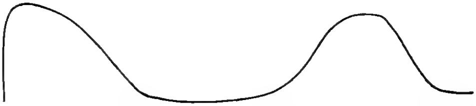

FIG. 104. Diagram from Dynamometer under Water.

It was found that with a slow explosive, such as gunpowder, the effect, as might be expected, varies inversely with the square of the distance, but with more brisant explosives it falls off much more rapidly, and with picric acid it is nearly inversely proportional to the fourth power of the distance. For instance, when the distance is increased from 4 to 5·5 metres, the effect, if proportional inversely to the square, would fall to 53 per cent. of its former value. Those actually measured were:

Gunpowder . . .	50–55 per cent.
Gel. VIII. . . .	46–48 ,,
Extra dynamite . .	40 ,,
Bellite	36 ,,
Gun-cotton . . .	30 ,,
Picric acid . . .	28 ,,

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[1] *Sixth Int. Cong. Appl. Chem.*, vol. 2, p. 612.

CHAPTER XXXI

IGNITION AND DETONATION

Development of explosion : Initiators : Fulminates and azides : Effect of moisture : Density and heat of formation : State of division : Manufacture of caps, etc. : Precautions : Wet process : Dry process : Drying : Drum method : Jelly-bag method : Charging : Pressing : Varnishing : Inspection : Official definition : Testing caps : Percussion primers : Friction tubes : Electric tubes : Igniters : Detonators and caps for shell fuses : Detonators or blasting caps : Packing : Composition of charge : Composite detonators : Boosters : Detonation of H.E. shell : Precautions : Disposal of waste : Testing detonators : Nail test : Sand test : Esop's test : Sound tests

Development of explosion.

In the last chapter it was shown how explosions vary in power and violence. In this one the development of the explosive wave will be discussed and the methods of initiating it. When an explosive, such as a smokeless powder, is "ignited," it burns from the surface inwards in parallel layers with a velocity which depends upon the pressure, but even under several thousand atmospheres never exceeds a few metres per second : the ignition is communicated from layer to layer by the heat generated. On the other hand, when an explosive is detonated the wave of detonation proceeds apparently through the mass of unaltered explosive with a velocity of several thousand metres per second, changing the material as it proceeds : in this case the explosion is communicated by pressure, but possibly this pressure acts by suddenly raising the temperature by compression.

A mechanical mixture of different substances, no one of which is able to explode by itself, such as black powder, cannot be made to detonate properly, because the chemical change can only take place at the points where the oxidizer and the combustible substances are in contact. Even under the most severe conditions as to pressure and initial shock the velocity of explosion does not exceed about 300 metres per second. But if saltpetre be replaced by potassium chlorate, which can be detonated, even when not mixed with combustibles, the case is quite altered and a high explosive is obtained, the velocity of detonation of which is several thousand metres per second.

When gunpowder is ignited it burns very rapidly, even if unconfined. The porosity of even highly compressed powder facilitates the spread of the flame. The rate of burning is affected comparatively little by pressure: hence the use of fine grain powder to ignite cannon cartridges.

Nitric esters, such as nitro-glycerine and gun-cotton, do not attain a very high rate of combustion when unconfined, unless in a state of fine division. This is apparently due to the fact that under these conditions the decomposition takes a different course from that which is followed when they are exploded in a confined space: the nitrogen is mostly set free in the form of nitric oxide or peroxide, and the heat liberated is very much less.

Initiators.

In the early days gunpowder was always ignited by means of a flame; later sparks from a flint and steel were utilized to light a priming of mealed powder, which communicated the flame to the charge. Not until the nineteenth century was use made of small quantities of sensitive explosives that could be ignited by a blow. It was the discovery of fulminate of mercury, which rendered this possible, and this substance is still an essential constituent of most cap compositions. When used by itself in sufficient quantity to ignite gunpowder with certainty, the fulminate produces such a sudden pressure that it deforms the cap. Therefore it is mixed with other substances which diminish violence and at the same time increase the heat of explosion. Saltpetre, sulphur and mealed powder were formerly added, but now potassium chlorate and sulphide of antimony are usually employed; some cap compositions contain all these constituents. Ground glass has also been used to increase sensitiveness, but it is not necessary when fulminate is present, and being chemically inactive, it, of course, diminishes the power of the cap. For use with smokeless powders, cap composition should not contain more than about 20 per cent. of fulminate of mercury, otherwise the pressure generated will be too high. Numerous attempts have been made to devise cap compositions containing no fulminate, such as a mixture of chlorate of potash and sulpho-cyanide of lead, but although a considerable degree of success has apparently been achieved, such compositions have not come into general use, probably on account of the difficulty in attaining the uniformity necessary with mixtures containing no one constituent which is both sensitive and explosive, especially as mixing by grinding is from the nature of the mixture impossible.

In the case of ordnance the conditions are somewhat different from those in small-arms: a larger quantity of material can be used, and a greater amount of force is available. Compositions can therefore be used containing no fulminate. They usually consist of potassium chlorate and antimony sulphide, together with a little sulphur to facilitate ignition and some glass powder to increase sensitiveness. The flash from this is communicated to some black powder, which in turn ignites the cartridge.

For the ignition of powders in fire-arms, heat only is required; for the detonation of high explosives, on the other hand, a very sudden and intense blow is necessary, and this can only be obtained by means of an explosive which itself detonates with a velocity of several thousand metres per second. Detonators are always fired by means of heat supplied either by a burning fuse or by a priming ignited by an electric current. When a light is applied to fulminate, at first it only burns with a velocity of about 10 metres per second, but the reaction becomes more and more rapid, and within an interval of time which is probably not more than $\frac{1}{3000}$th of a second, detonation sets in. The transformation of combustion into detonation has been shown experimentally in the case of explosive gas mixtures, and may be clearly seen in the photograph by Dixon reproduced in Fig. 105. This is a reproduction of a photograph taken on a film travelling rapidly in the direction, *b* to *a*. The object photographed was a glass tube, *ac*, containing a mixture of cyanogen and oxygen. The mixture was ignited at the end, *a*, by means of an electric spark; ignition proceeded with a moderate and fairly uniform velocity for a short time, then the velocity increased, and at the point, *b*, detonation suddenly set in, and then the detonation wave travelled on to the end, *c*, of the tube with a uniform velocity of several thousand metres per second. The detonation set in so violently that there travelled back from the point, *b*, a wave of compression, which was sufficiently powerful to raise the gas again to incandescence. This wave, which is called the "wave of retonation," moves with a velocity slightly less than that of the wave of detonation. From the end, *c*, of the tube the wave of detonation also is reflected back with somewhat lower velocity.

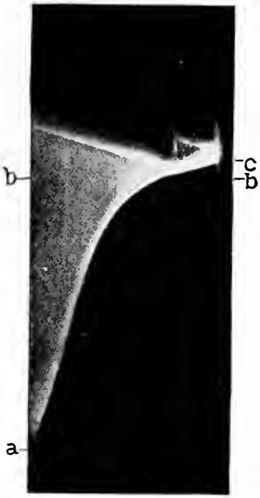

FIG. 105. Explosion of Mixture of Cyanogen and Oxygen (Dixon)

When a sensitive solid explosive, such as fulminate of mercury, is ignited, it probably behaves in much the same way as a gaseous mixture, but the transition from burning to detonation is so rapid, and takes place in such a minute space, that it cannot be followed.

An explosive can be used successfully to initiate detonation only if, after ignition, it detonates within a very short interval, and before any considerable quantity has burnt away. That is to say, the distance, *ab*, which in the case of the gas mixture shown in Fig. 105 amounts to several decimetres, must not be more than a few millimetres, or preferably only a fraction of a millimetre. Recent developments in the manufacture of detonators are due to no one more than to Professor L. Wöhler, who has investigated a number of different explosives with regard to this property. He calls it initial velocity,[1] but it is really acceleration and not velocity. In 1907 he published, together with O. Matter, the results of experiments with a number of sensitive explosives.[2] The following were some of the figures obtained :

	Density	Relative power in lead block c.c.	Temperature of ignition
Silver azide	3·38	22·6	290°
Mercury fulminate	3·37	25·6	190°
Chlorato-trimercuraldehyde	3·00	15·3	130°
Diazobenzene nitrate	1·46	43·1	90°
Nitrogen sulphide	2·11	39·2	190°
Sodium fulminate	1·65	14·9	150°
Basic mercury nitro-methane	2·45	7·5	160°

The power was determined in each case with 2 g. compressed into a detonator tube and fired with safety fuse in a lead block considerably smaller than that used for blasting explosives. Similar tubes were also fired standing on small lead plates : the results were in the order of the above list, silver azide perforating the plate most. Of all these explosives silver azide, mercury fulminate and the aldehyde are the only ones that have a sufficiently high acceleration to be of any use as initiators of detonation, and the azide is much more effective than fulminate of mercury. The aldehyde is too sensitive to be of practical use. It was made evident that the capacity to initiate detonation depends little, if at all, on the sensitiveness either to heat or to mechanical influences. The effectiveness of the substances as initiators was ascertained by first placing a quantity (usually 1 g.) of an insensitive explosive in a tube, gently pressing it down, then putting in a small quantity of the initiator and pressing the whole down with a pressure of 2000 kg. per sq. cm. It was finally fired on a lead plate to see if the detonation of the explosive was complete. By varying the quantity of initiator the minimum quantity was ascertained which would bring about detonation under these conditions :

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[1] Anfangsgeschwindigkeit, *see Ang.*, 1911, pp. 2089–2099.

[2] *S.S.*, 1907, pp. 181, 203, 244, and 265.

Explosive	Minimum weight of initiator (grammes)	
	Silver azide	Mercury fulminate
Gun-cotton	< ·05	·2
Picric acid	·024	·25
Trinitro-resorcinol	·08	·2
Trinitro-cresol	·05	·3
Trinitro-benzoic acid	·1	·25
Trinitro-benzene	·05	·25
Trinitro-toluene	·05	·3
Trinitro-xylene	·25	·4

The following figures were obtained by placing 0·5 g. of the nitro-aromatic compound in a detonator tube, then various quantities of the initiators with an inner capsule and compressing at 1100 kg. per sq. cm.:[1]

Initiator	Minimum charges for detonating			
	Tetryl	Picric acid	Trotyl	Trinitro-anisole
Mercury fulminate	·29	·30	·36	·37
,, ,, + 20 per cent $KClO_3$	·20	—	·30	—
Cadmium fulminate	·008	·05	·11	·26
Silver fulminate	·02	·05	·095	·23
Mercurous azide	·045	·075	·145	·55
Lead azide	·025	·025	·09	·28
Silver azide	·02	·035	·07	·26
Cadmium azide	·01	·02	·04	·10

Detonators constructed on this principle are now manufactured extensively. At first picric acid was used in combination with fulminate, but now trinitro-toluene or tetranitro-methylaniline are employed. The latter is the most effective, but it is more expensive than trinitro-toluene and somewhat more sensitive. The firm of Allendorff, for instance, makes a No. 8 detonator containing 0·7 g. trinitro-toluene covered with 0·5 g. of fulminate of mercury. This is fully equal to the usual charge of 2 g. fulminate and chlorate.[2] Un-

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[1] F. Martin through A. Stettbacher, *S.S.*, 1914, p. 356.

[2] *S.S.*, 1907, p. 5.

fortunately, fulminate is liable to deteriorate on keeping, and with such a small quantity as 0·5 g. the decomposition of a small proportion is likely to be more harmful than when there is a larger quantity present originally. Lheure[1] found that detonators containing picric acid and fulminate were more irregular than those charged with fulminate alone.

Fulminates and azides.

In a later communication[2] Wöhler discusses other substances that may be used as initiators of detonation, especially the various azides. Those of silver, copper and lead have such high auto-acceleration that they develop their full effect even when quite unconfined, and the same applies to nitrogen iodide, which, however, is so sensitive that it is exploded by a touch. Fulminate of mercury does not produce its full effect when quite unconfined, but a thin copper capsule provides sufficient confinement. The difference in the rates of acceleration is shown by exploding a small quantity in a test-tube: fulminate of mercury does not injure the tube, whereas fulminate of silver pierces it, and azide of silver shatters it to a thousand fragments. These results are in accordance with the results of tests carried out to ascertain the minimum amounts required to detonate trinitro toluene:

Mercury fulminate	·25 g.
Silver fulminate	·15 g.
Lead azide	·05 g.
Silver azide	·02 g.

The divergence between these figures and those quoted above is probably due to smaller compression of the explosives. Storm and Cope[3] found that the following quantities of fulminate-chlorate mixture were required by three different samples of trotyl according to the compression:

Pressure	Sample 1	Sample 2	Sample 3
400 atm.	0·25 g.	0·29 g.	0·31 g.
300 "	0·25 g.	—	—
200 "	0·24 g.	0·23 g.	0·24 g.
100 "	0·23 g.	—	—
50 "	0·19 g.	—	—

The quantity of priming required also depends on the physical condition of the secondary explosive, especially on the size of the particles; the finer it is pulverized, the less priming is required.

G. B. Taylor and W. C. Cope[4] obtained the following results in tests to

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[1] *P. et S.*, vol. xii., p. 134.

[2] *Ang.*, 1911, p. 2089. *See also* further communication by Wöhler and Martin, *S.S.*, 1914, p. 242; *Ang.*, 1914, vol. i., p. 335.

[3] *U.S. Bureau of Mines Technical Paper*, No. 125, p. 49.

[4] *U.S. Bureau of Mines Technical Paper*, No. 145.

ascertain the quantity of fulminate of mercury composition required to detonate mixtures of trotyl and tetryl:

Trotyl	Tetryl	Fulminate required
100 per cent.	0 per cent.	0·25 gramme
90 ,,	10 ,,	0·22 ,,
80 ,,	20 ,,	0·21 ,,
50 ,,	50 ,,	0·20 ,,
0 ,,	100 ,,	0·19 ,,

In these tests 0·4 gramme of the explosive was placed in a detonator tube, varying quantities of a mixture of 90 per cent. fulminate and 10 per cent. potassium chlorate was placed on top, a thin copper reinforcing cap 9 mm. long with a perforation 2·3 mm. in diameter was inserted and pressed down for one minute under a pressure of 200 atmospheres (206 kg./sq. cm.).

Lead azide is now used as a substitute for fulminate for the manufacture of detonators. As long ago as 1893 experiments with the azides of silver, lead and mercury were started at Spandau by the Prussian Government, and met with considerable success, but they were stopped in consequence of a man being killed by an explosion. Lead azide is considerably less sensitive than fulminate of mercury, provided that it be in a fine state of division, but unlike the fulminate it can be obtained in crystals of a considerable size, and these are much less stable. It is indeed a general rule that the sensitiveness to shock increases with the size of the crystals. The material is evidently in a state of great strain; the strong double refraction of the crystals of all these "initiators" confirms this. Mercuric azide, for instance, when in crystals measuring 0·6 to 0·9 mm., is not much more sensitive than mercuric fulminate, but if the crystals are allowed to grow to 3 mm. diameter, it is liable to explode spontaneously even under water. Lead azide is made by the double decomposition of sodium azide and lead acetate, and the size of the crystals of the precipitated lead azide depend on the temperature. In 1910 in Germany a man was killed in a factory by the explosion of some lead azide under water, and there have been other fatal accidents.[1]

The azides are not so brisant as the fulminates. It is possible to combine the high acceleration of the former with the brisance of the latter by the use of a combined charge. Thus fulminate of mercury to which a centigramme or less of lead azide has been added is even more effective in detonating trinitrotoluene than the azide itself. Diazo-benzene nitrate also, which is of but little use itself as an initiator of detonation, becomes very effective by the addition of a centigramme of lead azide.

Wöhler has determined the sensitiveness of many of these substances both to temperature and to the falling weight:

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[1] S.S., 1911, p. 417.

	500 g. weight falling mm.	Temperature of ignition
Mercury fulminate	75–100	200°
Silver fulminate	140	200°
Sodium fulminate	over 320	150°
Mercuric azide (crystals ·6–·9 mm.)	65	200–210°
,, azide (,, 3 mm.)	0	200–210°
Mercurous azide	200	300°
Silver azide	310	200°
Cupric azide	0	200–210°
Cuprous azide	260	200–210°
Lead azide (finely divided)	260	340–350°
,, azide (moderate crystals)	130	340–350°
Basic lead azide	280	380°
.. cupric azide	315	245°

Wöhler suggests that the basic azides may be used in cap compositions instead of fulminate. They have comparatively low accelerations, and consequently are not so liable to deform the cap or give high pressures in the fire-arm. The sensitiveness both to blows and to temperature depends upon the conditions under which the tests are carried out. Martin using the same apparatus as Wöhler and Matter for determining the temperature of ignition obtained the results below. A small quantity of the explosive was placed in a thin copper tube, which was immersed for about half a minute in a bath of molten Wood's metal. If there was no explosion in this time the temperature was increased 5°. and the experiment was repeated until an audible explosion was obtained.

Mercury fulminate	186°
Cadmium fulminate	210°
Silver fulminate	170°
Sodium fulminate	215°
Mercurous azide	291°
Lead azide	327°
Silver azide	297°
Cadmium azide	281°

With a 700 g. pendulum the following figures were obtained for sensitiveness:

Fulminate of mercury alone	100–120 mm.
80 per cent. fulminate, 20 per cent. pot. chlorate	220–260 mm.
Lead azide	230–260 mm.

Exposure to light was not found to increase appreciably the sensitiveness of azides either to blows or heat:

	Falling pendulum mm.		Temperature of ignition	
	Unexposed	Exposed	Unexposed	Exposed
Silver azide . . .	315	315	300°	305°
Mercurous azide . . .	200	180	295°	330°
Lead azide . . .	210	205	345°	345°
Lead azide under water .	above 315	above 315	—	450°
Basic lead azide . .	280		390	—

The falling weight tests were carried out with 0·05 g. of dry finely powdered substance pressed at 2460 kg. per sq. cm. The weight of the falling pendulum was 600 g. except in the case of the silver salt, where it was 640 g.[1]

One of the disadvantages of fulminate of mercury is that it deteriorates on storage, especially if the temperature be high or the atmosphere moist. In Austria there is an official regulation that detonators are to be stored over fused calcium chloride.[2] Different lots of fulminate differ considerably as to their liability to deteriorate, but this matter does not appear to have been studied very much. Lead azide is much more permanent. This is clearly shown by the photographs by Wöhler reproduced in Fig. 106: originally, of course, detonators of both descriptions perforated the lead plates.

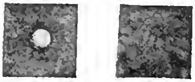

FIG. 106. Effect of Detonators on Lead Plates after keeping in Moist Atmosphere 200 Days

A. Charged with Lead Azide.
B. Charged with Mercury Fulminate and Potassium Chlorate.

The lead azide is generally used in conjunction with tetryl (tetranitromethyl-aniline) or trotyl (trinitro-toluene). The latter is put into the copper capsule first and pressed down, then the azide, and over that a reinforcing cap of copper with a central perforation, and the pressing is repeated. The cap, which is also used in fulminate composite detonators, is to prevent the upper layer of explosive falling out and to protect it from moisture,[3] and to increase the effect of the fulminate.

Effect of Moisture.

In further tests it was found that detonators charged with fulminate or fulminate-chlorate mixture entirely lost their effectiveness after keeping for thirty days in a saturated atmosphere, whereas lead azide detonators were still quite good after 900 days, and the same applied to detonators charged with tetryl and a small quantity of lead azide. One per cent. of water in the fulminate rendered it useless, but five per cent. made no perceptible difference to the

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[1] *S.S.*, 1914, p. 391.

[2] *See S.S.*, 1909, p. 38.

[3] Neitzel, *S.S.*, 1913, p. 171.

azide.[1] Storm and Cope, however, found that 0·75 per cent. of moisture had no appreciable effect on a No. 7 detonator charged with 90/10 fulminate mixture.[2]

Other Initiators.

Many other explosive substances have been proposed as initiators, but have not achieved any practical success up to the present. E. Herz has taken out a patent [3] for the perchlorates of the diazo-compounds, especially that of nitro-bisdiazo benzene $C_6H_3NO_2(N:N.ClO_4)_2$. It is claimed that this substance is stable and even more effective than the azides. A quantity of 0·015 to 0·02 g. suffices to detonate picric acid, but it is necessary to separate the substances with a thin tin or copper disc as they react on one another. Another purely organic initiator that has been proposed is hexamethylene-triperoxide-diamine, which has been patented by von Girsewald.[4]

Density and heat of formation.

The effectiveness of fulminate of mercury as an initiator has often been ascribed to its high specific gravity of 4·4, and this view appears to receive confirmation from the fact that other substances that can be used instead are many of them compounds of heavy metals and also have high specific gravities. Fulminate of mercury, however, is generally only compressed into detonators at about 250 kg. per sq. cm., and then only has an apparent density of about 2·2, which is not very much more than that of many other explosives which could not possibly be used as initiators. If the pressure exceed 700 kg. per sq. cm. the effectiveness is diminished. In this respect it differs from lead azide, which is improved by increasing the pressure at any rate up to 10,000 kg. per sq. cm.[5] Although great brisance is a desirable quality in an initiator, and this is increased by raising its density, rapid acceleration of detonation is far more important, and this is diminished in the case of fulminate by too much compression. For an explosive to have a high auto-acceleration of detonation it appears to be necessary for it to be an endothermic compound and for its heat of formation to have a considerable negative value. The following are a few instances :

Explosive	Formula	Heat of Formation	
		Cals. per mol.	Cals. per kg.
Mercury fulminate . . .	$Hg(CNO)_2$	— 62·9	— 221
Silver fulminate . . .	$AgCNO$	— 44·4	— 296
Lead azide	PbN_6	— 105·9	— 364
Nitrogen chloride . . .	NCl_3	— 38·5	— 320
Nitrogen sulphide . . .	NS	— 31·9	— 692
Diazo-benzene nitrate . .	$C_6H_5.N:N.NO_3$	— 44·9	— 269

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[1] S.S., 1914, p. 393. [2] *U.S. Bureau of Mines Technical Paper*, No. 125, p. 62.

[3] Germ. Pat. 258,679, April 27, 1911.

[4] Germ. Pat. 274,522, September 14, 1912. [5] S.S. 1914, p. 392.

Substances with large negative heats of formation are not, however, necessarily sensitive explosives. Cyanogen, C_2N_2, for instance, has a heat of formation of −68·5 Calories per mol. or −132 Calories per kg. in the liquid state, yet it can only be detonated with difficulty and does not explode at all on heating. The cyanides of the heavy metals are also endothermic compounds, but are not explosive under any ordinary circumstances. In these cases the substances probably become more stable at high temperatures or even exothermic. For an explosive to have the power of initiating detonation, although present only in a small quantity, it appears to be necessary not only for the molecule to be formed with the absorption of heat, but also for it to be in a state of internal strain. It is also of course essential that gaseous products be formed in its decomposition.

State of division. The properties of initiators depend to a considerable extent on their state of division. This does not affect their sensitiveness to heat, but to blows large crystals are far more sensitive than small ones, and the sensitiveness of the fine crystals can be further reduced by powdering them. The sensitiveness to detonation takes the opposite course, and is greater for the fine material. Consequently the auto-acceleration of detonation is greater in fine material, which is therefore more efficient as an initiator. According to Wöhler if fulminate of mercury be dissolved in potassium cyanide solution, and then be reprecipitated in a very fine condition by means of acid at 0°, only a third as much is required to detonate explosives as if the original fulminate were used.[1]

Contact. Both in the design and use of detonators care should be taken that the contact between the different explosives is as close as possible. An interval of even a twentieth of an inch (or a millimetre) between the detonator and the explosive to be detonated greatly diminishes the effect. The top part of the fulminate, where it is ignited, is not so effective as the lower part, where it has its full velocity of detonation. In the case of caps for igniting propulsive explosives intimate contact should be avoided, as what is required then is ignition by means of a flame.

MANUFACTURE OF CAPS, DETONATORS, ETC.

Precautions. Special precautions must be observed when dealing with the very sensitive substances used for charging caps, detonators and other igniters; there is far more danger of explosion than there is with other commercial explosives. The danger is diminished by restricting the quantities that are allowed to be present in any one building. As the amount of explosive in each cap or detonator is small, this restriction does not interfere seriously with the work. The total quantities dealt with are not small, however, for it is estimated that 100 tons of fulminate of mercury are made in Germany every year, and a single

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[1] *Ang.*, 1911, p. 2095.

factory in Great Britain manufactures more than double this quantity. The various constituents, before mixing, are sifted through fine sieves to remove all gross gritty particles. The fulminate and the explosive mixtures are kept and transported in small boxes of papier mâché or other soft smooth material. In those buildings where quantities of a pound or more may be present *en masse*, the floors should be covered with linoleum or other soft stuff, and the workers should all wear felt slippers or only socks. The greatest cleanliness should be observed.

The mixing and drying operations are specially dangerous. The mixing of the composition was at one time done in a very simple way by placing the ingredients on a piece of paper and then stirring them with a goose feather, or by lifting first one corner of the paper and then another. Under these conditions it was never possible to protect the worker adequately, and with such very sensitive material there is always danger of an explosion. Now the mixing is either carried out wet, or it it done in a "jelly-bag."

Wet process.

The wet process of mixing has been described in detail by Hagen:[1] its essential feature is that the explosive is kept wet until the mixing is complete. As the ingredients tend to separate from one another when wet, even more than when dry, in consequence of the differences in their densities, it is necessary to incorporate with them a binding material, usually gum arabic, although Alden uses gelatine. The fulminate and other constituents are mixed together by hand in a basin with just sufficient of a 6 to 7 per cent. solution of gum arabic to wet it thoroughly. Then the mixture is granulated by pressing it through first a sieve with about 6 meshes to the inch, and then one with 15 meshes. By official order these sieves must be of hair or silk. The granulated composition is dried at a temperature of 30° to 35°; then it is sifted, and that portion is selected which passes a 50-mesh sieve and is retained by a 120; this constitutes about 60 per cent.; the remainder is returned to the granulating house, where it is moistened again and mixed with fresh composition.

Only just enough water should be used thoroughly to moisten the mixture, so that when it is worked it is formed into a uniform thick mud. This is not very easy, and in spite of precautions some of the composition is liable to get dry. If it be too wet, the liquid will carry away some of the potassium chlorate and other soluble constituents. Alden overcomes this difficulty by adding alcohol, which reprecipitates the chlorate, and also the gelatine which carries down with it all matter in suspension, and so clarifies the liquid. The cap composition for the Austrian military rifle is made as follows: 540 g. of finely ground and sifted potassium chlorate are placed in a basin, and 284 c.c. of a 3 per cent. solution of gelatine are added, and they are stirred

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[1] S.S., 1911, pp. 201, 224, 243, 265, 283 [illegible] 308.

together until all lumps have been broken up. Then 210 g. of wet fulminate, containing 15 per cent. of water, are stirred in, and finally 435 g. of antimony sulphide and 140 g. glass powder. Then 500 g. of 95 to 96 per cent. spirit are poured in, and the liquid is allowed to settle. The composition is filtered off on a fine double cloth, allowed to drain, pressed down, and then squeezed out by two girls, who twist round the two ends of the cloth.

The wet process suffers under the disadvantage that the workers are constantly manipulating considerable quantities of composition, and, although the material is kept wet most of the time, ignitions are not uncommon.

At one time wet composition was loaded directly into the caps by some makers. This method had the advantage that dry composition did not have to be manipulated in bulk at all. But when it dried in the cap it formed a hard mass, which was sometimes exceptionally sensitive and led to accidents.[1] Friction tubes for ordnance are still sometimes loaded by this method, but the compositions for these generally contain no fulminate.

Dry process.

Fulminate, which is always stored wet until actually required, must, of course, be dried before mixing by the dry process.

Drying.

The drying is carried out in an isolated building, where the wet fulminate is spread out on soft fabric. The building is heated by means of hot-water pipes to a temperature of 30° to 35°. The drying occupies only a few hours, as the fulminate is not at all hygroscopic. Then the building is allowed to cool down: on no account should the fulminate be touched until it is quite cold, as its sensitiveness increases with the temperature.

The drying is also carried out sometimes in vacuum drying ovens.

Drum method

In some Continental factories the mixing is carried out in drums of papier mâché 40 cm. in diameter and 15 cm. thick.[2] Two of these rotate within a strong enclosure. In the first all the constituents, with the exception of the fulminate, are mixed together, soft rubber balls being added to the charge to assist the mixing. The axle is turned for a few minutes by hand from behind a protecting wall. Then the contents of the drum are emptied out through a funnel and a coarse sieve, which retains the rubber balls but allows the composition to pass through. The fulminate is then added to this, and the mixing is repeated in the same way in the other drum, which, however, contains no rubber balls. Each charge is about 250 g.

Jelly-bag method.

The "jelly-bag" method originated in France, but is now generally adopted in Great Britain also. The plant is shown in Fig. 107. The various constituents, amounting altogether to ½ lb. to 2 lb., are put into the silk bag, the fulminate last. Then the workman retires behind the screen and works the lever for about three minutes to effect the mixing. Then the lever is drawn right down, so that the bag is turned inside out, and the mixed composi-

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[1] *See S.R.*, No. 113, para. 13.

[2] *See* Knoll, *Knallquecksilber*, p. 153.

tion falls through the leather funnel into a small box standing on the bracket just below it. Explosions have occurred in this plant occasionally, but have only done very slight damage, and the workman has always escaped injury. The machine is generally arranged, however, so that he is further removed from the explosive than is shown in the figure. Mechanical power is now often substituted for hand labour, as the mixing is then more uniform. Instead of the rubber rings soft rubber balls are used; they are placed loose in the bag, and are separated afterwards by means of a coarse sieve. Over the top of the plant a cotton sheet should be suspended to make sure that nothing can fall into the bag.

The ingredients are not mixed together very intimately, but this is no disadvantage, as the violence of the caps is thus diminished.

Charging. The charging and pressing of the caps is performed in machines such as those made by Greenwood and Batley, of Leeds. The capsules are made of copper, more rarely of brass; they are punched out of sheet metal and pressed to the required shape. The permissible variations in dimensions are very small. They are then lacquered with varnish to prevent actual contact between the composition and the metal. The capsules are filled into a plate or " hand " which has a large number of depressions, each just large enough to take a capsule: there may be as many as 1000 of these depressions, 40 rows of 25 each.

The charging machine consists essentially of several brass or bronze plates, each perforated with a number of holes corresponding to the depressions in the " hand." The holes in the top plate are just large enough to take the quantity of composition required for one cap.

A little more than enough composition to fill all the caps is placed on the plate, and then with a piece of soft cloth or rubber the worker passes it over the plate and so fills all the holes. As the charge of each cap is only 0·3 to 0·6 grain (0·02 to 0·04 g.), the total quantity of explosive is not much more than 40 g., and the explosion of this would not do very serious damage, provided it be not allowed to spread to more composition. The stock of composition must therefore be kept in a safe place at some little distance. By a slight movement of the second plate each charge is now caused to fall into its cap. This movement is produced by means of a long rod, so that the worker is not near the explosive.

Pressing. The charges have next to be pressed. This is carried out in a machine which has a row of pistons, that are made to descend on to the caps. Each piston is weighted with a separate weight, connected to it through a system of levers so that not more than a certain pressure, say 2 cwt., can be exerted on each cap. When one row of caps has been pressed, the hand moves forward automatically so as to bring the next row under the pistons.[1]

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[1] *See also* Hagen, S.S., 1912, pp. 277, 297, 322, 343, 367, 388, 411, 431, and 449.

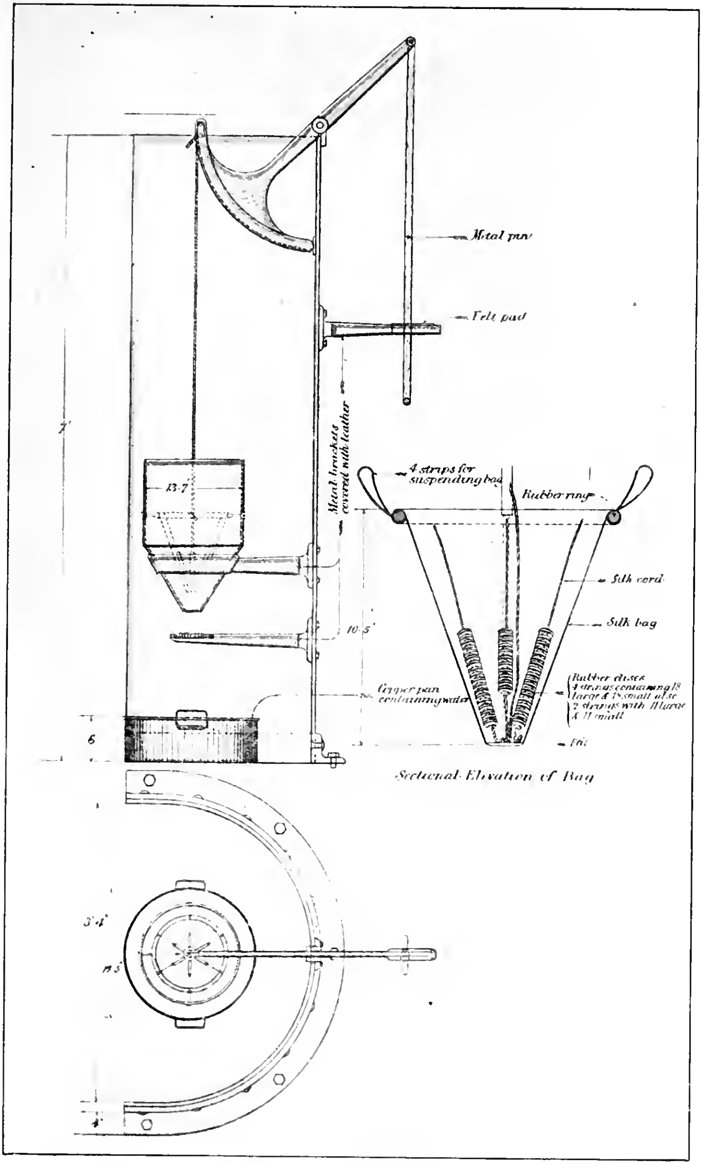

FIG. 107. Jelly-bag Plant for Mixing Fulminate Compositions

Varnishing. Any loose composition is now removed by exposing the caps to a mild blast of air in a special cupboard, which should be so arranged that the composition carried away by the air is caused to fall into a pan of water. Then the composition is varnished. This operation is performed in an apparatus which has a number of pins projecting vertically downwards from a movable horizontal plate, one pin for each cap in a hand. The plate is brought down until the pins dip into a shallow trough containing a solution of shellac in spirit. Then it is raised again and a hand of caps is slipped under it, and it is brought down again so that a small drop of varnish is deposited in each cap. The caps are then removed from the hand and dried at a gentle heat to remove the alcohol, and finally they are drummed or "rumbled" in order to clean them. They are then ready to insert into the cartridge cases.

The composition in each cap is frequently covered over with a small disc of tin-foil. This is essential if the caps are not to be loaded into cartridge cases in the same factory, because otherwise there is danger of some of the composition escaping. Not only would this make the caps unreliable, but the loose composition would render them liable to explode in bulk. There are two ways in which the tin-foil may be introduced. One way is to stamp the foil from a sheet straight into the caps in a special machine. In the other method a lot of discs of foil are placed in a tray, down on to which is brought a plate bearing a number of little vertical tubes. A vacuum is applied to these so that each picks up a disc. The hand is then slipped under it, the plate is again brought down, the vacuum is released, and so a piece of foil is introduced into each cap. The caps are then pressed again and varnished.

An alternative scheme of working is as follows: [1] The composition receives a preliminary pressing, the excess of composition is blown off, and foil having still moist varnish on its under side, is stamped straight into the caps, which then receive their final pressing. This method is used when the composition has binding material incorporated with it by the wet process. Finally the caps are drummed and sifted so as to remove all loose composition.

Inspection. During and between all the operations careful supervision is necessary to make sure that no defective caps pass through the process, for a missfire is always annoying and may be dangerous, and irregularity in the charges of the caps leads to unevenness in the ballistics of the cartridges.

When used in rifles foiled caps are liable to cause fouling of the rifling, unless there be sufficient excess of oxygen in the composition to oxidize the metal of the foil completely. The effect produced by the cap depends upon many circumstances: the nature of the powder, the nature and quantity of the composition, and the way in which it has been mixed and pressed, the shape and size of the cap chamber and the anvil on to which the cap is knocked by the blow of the hammer or bolt, and the size of the fire-holes through which the products of the cap impinge on to the powder. All these factors combine

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[1] *See* Knoll, *Knallquecksilber.*

together to cause the more or less rapid ignition of the powder, and consequently it is not possible to specify any one composition as the best under all circumstances. Mixtures of fulminate, potassium chlorate and antimony sulphide are used almost exclusively, although there are serious objections to all three substances. The fulminate is dangerous and expensive; it deteriorates on keeping, especially when moist, and on explosion it gives metallic mercury, which injures the brass of the cartridge case, so that it cannot be used again for the same purpose. The antimony from the sulphide is also injurious to the brass, and the chlorate forms chlorides, which cause the barrel to rust, unless it is cleaned thoroughly after firing. There are many other mixtures that can be employed, but apparently none of them is sufficiently reliable and satisfactory for general use. Of the oxidizing agents available, saltpetre cannot be used because it is too hygroscopic, but it is not easy to see why barium nitrate cannot be substituted for potassium chlorate. As combustibles the following have been used or proposed: lead ferrocyanide, copper ammonium thiosulphate,[1] lead sulphocyanide, mercury sulphocyanide, metallic aluminium, sulphur, sodium azide.[2] As substitutes for the fulminate, Wöhler has proposed the use of basic azides. Use has, however, sometimes been made of mixtures containing no substance which is a sensitive explosive by itself. The United States, for instance, have used for their small-arms a mixture of potassium chlorate 47·2 per cent., antimony sulphide 30·8 per cent., sulphur 22 per cent.

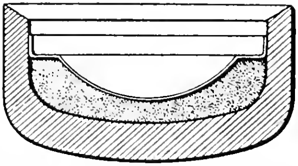

FIG. 108. Percussion Cap for Cartridge of Mannlicher Rifle. Magnified 10 Diameters

The following are some fulminate compositions that are used:

	Austrian (Hagen)		English Small-arms	
	Small-arm	Shot-gun	Gunpowder	Cordite
Mercury fulminate	13·7	33·9	37·5	19·0
Potassium chlorate	41·5	21·6	37·5	33·3
Antimony sulphide	33·4	—	25·0	42·9
Glass powder	10·7	43·2	—	—
Gelatine	0·7	1·3	—	—
Sulphur	—	—	—	2·4
Mealed powder	—	—	—	2·4

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[1] *See* Herz, S.S., 1912, p. 284.

[2] Winchester Repeating Arms Co., U.S. Pat., 1,184,316 of May 23, 1916.

The proportion of glass in the second mixture is very large: in England compositions for shot-gun caps often contain no glass powder.

The products of explosion of a composition should contain a considerable proportion of non-volatile solids, so that a high temperature may be produced combined with a low pressure.

Official definition. According to the ruling of H.M. Chief Inspector of Explosives, percussion caps must be of such strength and construction that the ignition of one will not ignite the others. Each cap must not contain more than 0·5 grain of composition (0·032 g.), which must be protected by a coating of tin-foil or other material approved by the Inspector, and it must not contain the anvil. If the proportion of fulminate in the composition does not exceed 25 per cent., the charge may be increased to 0·6 grain (0·039 g.). If these conditions are not fulfilled, the cap is considered to be a detonator, and must be packed and stored accordingly.

Testing caps. An old and simple method of testing percussion caps consists in flashing them against a piece of white paper from a fixed distance and comparing the marks made. This only affords a rough indication of the uniformity of manufacture. The pressure generated may be measured in the apparatus made by Cogswell and Harrison.[1] The cartridge case is screwed down on to a hollow steel rod, inside which works a piston. The other end of this piston bears against a small lead crusher. The cap is fired by dropping a weight from a known distance on to a striker. The pressure generated by the cap is then communicated to the piston, and the consequent diminution in the length of the lead cylinder affords a measure of the pressure. The same instrument can also be used to determine the energy of blow necessary to fire the caps properly. Brownsdon[2] has given a number of methods for examining caps. The flash may be photographed, and the results are often instructive. The volume of gas generated can be measured by firing the cap in a closed chamber, and at the same time an indication of the amount of heat liberated can be obtained by having a delicate thermometer projecting into the chamber, and reading the rise of temperature. The time of flash was estimated by flashing caps towards a rotating disc pierced with a number of holes, behind which was a camera focused on to the disc. From the length of the marks made by the illuminated holes, and the known velocity of rotation, the duration of the flash could be calculated: it was estimated to be about $\frac{1}{\text{[illegible]}}$th of a second.

The methods have been further developed by Borland.[3] He estimates the length and duration of flash by firing a cap in front of a slit behind which a photographic plate is revolved, thus obtaining a V-shaped image. The

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[1] *See* Guttmann, *Manufacture*, vol. ii., p. 369.

[2] *J. Soc. Chem. Ind.*, 1905, p. 381.

[3] *J. Soc. Chem. Ind.*, 1906, p. 241.

heat generated he measures by firing against a thermocouple, instead of a thermometer. The temperature of the flash was measured directly, by means of an optical pyrometer, from the intensity of light in a selected portion of the spectrum. The temperatures recorded ranged from 1150° to 1520°, but when the caps were coated with aluminium powder temperatures of 1570° and 1690° were obtained. The temperatures as calculated with the aid of Mallard and Le Chatelier's specific heats were about twice as high, but in these calculations no allowance was made for heat lost by radiation and conduction and by the work done in the expansion of the gases. The results obtained with the optical pyrometer were found to be unaffected by considerable variations in the quantity of composition in the cap. An indication of the temperature can also be obtained by exposing portions of the same photographic plate to the flashes from different caps, and comparing the densities of the developed plates in a Chapman-Jones plate tester.

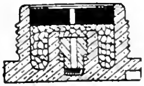

FIG. 109
Percussion Primer for Quick-firing Ammunition

Percussion primers.

For the percussion primers of quick-firing gun ammunition the conditions are somewhat different. First, there is more force available, and consequently the composition need not be so sensitive; and, secondly, the flash is not required to ignite the powder charge directly, but is first communicated to a small quantity of small grain black powder, which in turn ignites the cartridge; consequently these caps do not require to be so uniform in their effects as those used for small-arms. The compositions generally contain no fulminate, but consist principally of potassium chlorate and antimony sulphide. Fig. 109 shows the construction of a German percussion primer. The percussion cap is held in place by the screwed anvil, through which there is a perforation permitting the flash to ignite some fine grain powder. Over this there is a pellet of compressed powder, also with a central perforation, held in position by a disc of shirting and a brass plate with fire-hole, held down by the turned-over edge of the primer. After it has been assembled the primer is varnished.

Friction tubes.

The friction tubes for igniting gun cartridges that are not enclosed in metal cases are constructed on much the same principle, except that the pellet of composition is ignited by the friction of a bar or wire pulled or pushed through it, instead of by the blow of a striker or bolt. As the tube has to be inserted through a hole in the wall of the gun, it must be several inches long. The tube is filled with powder grains or pellets, which carry the flash well into the chamber of the gun. At the top of the tube is the pellet of composition, which is made of a mixture similar to that used for the percussion primers. Hagen gives the following figures for the composition used in friction tubes:

Potassium chlorate	66·2 per cent.
Antimony sulphide	33·1 ,,
Gum arabic	0·7 ,,

Half of the chlorate is only coarsely ground.

lectric tubes. Naval guns and guns of position are often fired electrically. For this purpose tubes are used in which the friction pellet is replaced by some priming composition, consisting of a mixture of mealed powder and gun-cotton dust, or other easily ignited material. Through this passes a short piece of fine platinum wire, the two ends of which are connected with two copper wires, which can be joined to the poles of a battery. The general construction of the electric tube resembles that of an electric detonator, except that the fulminate is replaced by black powder, and the tube is more solidly constructed. All igniting tubes, whether friction or electric, must be so designed that the powder gases cannot blow out through the outer end.

Igniters. The flame from the tube does not suffice, however, to ignite the cartridge, which consequently has to be provided with an igniter. This generally consists of fine grain black powder contained in a bag or pocket covering the end of the cartridge. The quantity is generally from ½ to 2 per cent. of the weight of the smokeless powder. There are various objections to the use of black powder for this purpose, and attempts have been made to find some other material that may be substituted for it. One objection is that this priming considerably increases the amount of smoke that is formed when the charge is fired. For guns of small calibre ungelatinized gun-cotton in the form of yarn is sometimes used, but no priming gives such regular ballistics as the black powder, especially in the big guns. Smokeless powders of small size have been tried, but not always with success.[1] Powder in the form of strip, tube or cord ignites more rapidly and uniformly than flake or cube powder, because in the former case the flame can spread without delay to the further end of the cartridge.[2]

Detonators and Caps for shell fuses. Fuses for shell contain percussion caps, which in the case of percussion fuses are fired by the shock of impact, and in the case of time fuses by the shock of discharge of the gun either directly or indirectly. Either a pellet carrying a needle impinges on the cap, or the cap mounted in a pellet impinges on a fixed needle. The caps are of copper and generally similar in form to those of small-arm cartridges, except that they are often perforated to allow the flash to escape in the opposite direction to the needle. The caps are usually filled with cap composition, more rarely with fulminate alone, and are then more accurately called detonators. Full details have been given by O. Hagne of the manufacture of caps for German fuses.[3] The caps for the ordinary

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[1] *See S.S.*, 1908, pp. 154, 285.

[2] W. Heydenreich, *S.S.*, 1906, p. 148.

[3] *S.S.*, 1915, p. 177, etc.

German time and percussion fuse is cylindrical, 4·7 mm. in external diameter, and 6 mm. high; in the base there is a hole 2·5 mm. in diameter. Into this is first placed a piece of copper foil, then 0·092 g. of a mixture of the composition:

Fulminate of mercury	16·0
Potassium chlorate	51·3
Antimony sulphide	32·0
Gelatine	0·7

Then a disc of tin-foil and the whole is pressed at 2·3 to 2·4 kg. per sq. cm., so that it occupies a height of 2·6 to 2·9 mm. in the copper cap. The total cost of these caps in normal times is stated to be 16·41 marks per 1000.

DETONATORS OR BLASTING CAPS

Detonators are manufactured in much the same way as percussion caps, but in consequence of the greater violence of the charge, and the far greater quantity in each, much more stringent precautions must be taken for the protection of the workers. The capsules are drawn copper tubes without joint, closed at one end. Of these 100 are placed in holes in a plate or "jig," which is often made of ebonite, the holes being lined with brass to prevent deformation. The capsules should fit the holes well but not tightly. This jig slides into the filling machine, which has two plates each pierced with the same number of holes as the jig. The lower of these plates is preferably made of ebonite and is of such a thickness that each hole contains just enough fulminate composition for one detonator. This plate is movable within certain limits, whilst the top plate is fixed. At one extremity of its travel the holes in the second plate come under those in the top plate, at the other end of its travel they come over the capsules in the jig. At first, however, the second plate is placed so that its holes are under those of the top plate. Dry fulminate, or fulminate mixture, is placed on the top plate in quantity rather more than sufficient to fill the 100 detonators, and is then gently swept into the holes; then the second plate is moved so that the fulminate falls into the capsules. These operations are carried out from behind a strong shield by means of rods passing through it, so that if the fulminate explodes, the worker will not be injured. The upper plate is then removed, and the surface of the jig is gently wiped down with a damp cloth to remove any loose explosive. The jig is then taken to the press, which has 100 small pistons fitting closely but not tightly into the capsules. The pressure applied to the fulminate is usually about 250 to 300 kg. per sq. cm. or 50 to 60 kg. on each detonator, which compresses the explosive to a density of about 2·2 to 2·6. If the density be raised by increasing the compression above 700 kg. per sq. cm., the fulminate becomes less sensitive, and consequently a larger quantity burns away before detonation sets in, so that although the brisance of the detonating portion is greater, the effectiveness of the whole detonator may be less. The variation of the density with the pressure was determined by Wöhler and Matter as also the power by exploding charges of 2 g. in lead blocks:[1]

Pressure kg cm²	Density	Trauzl test c.c.
100	1·92	30·6
400	2·56	28·5
800	2·98	26·0
1200	3·21	25·6
1600	3·23	25·4
2000	3·36	25·6

There is, of course, no direct connexion between the results of the Trauzl test and the effectiveness of a detonator, but the figures show how increase of density can have a bad effect. After pressing, the detonators are removed from the jig either by tipping it over into a pan containing sawdust, or by pushing them out from below. Then they are drummed, or "rumbled," and sifted, to remove the sawdust and all loose fulminate. During these operations also, the workers must be protected by strong shields.

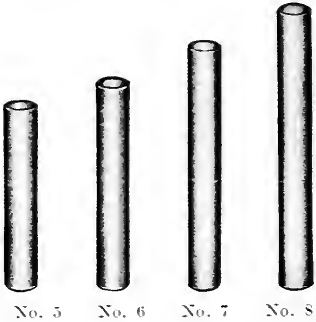

FIG. 110. Detonators

Packing.

Finally they are packed in tin boxes, each of which contains not more than 100. The boxes must be lined with paper or similar material, and there must be a pad of felt, cotton wool or other soft stuff against the ends of the detonators. The spaces between the detonators and in their open ends are filled with sawdust. These boxes are then packed in an outer package. If the number of detonators within the outer package exceed 1000, there must be a double outer package with a space of 3 inches everywhere between the two. If the number exceed 5000 the outer package must have handles to assist the moving. The maximum allowed in one outer package is 10,000.[2]

Detonators of different strengths are distinguished by numbers, which are the same in all countries:

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[1] S.S., 1907, p. 245.

[2] Explosives Act.

No.	Usual external dimensions of tube		Charge grammes
	Length mm.	Diam. mm.	
1	16	5·5	0·3
2	22	5·5	0·4
3	26	5·5	0·54
4	28	6	0·65
5	30–32	6	0·8
6	35	6	1·0
7	40–45	6	1·5
8	50–55	6–7	2·0
9	—	—	2·5
10	—	—	3·0

The following are the mean weights of charge (90/10 mixture) in a number of American detonators and the results obtained in the "sand test":[1]

Grade No.	Weight of charge grammes	Sand Test Per cent. passes 30 mesh
3	0·495	22·0
4	0·636	27·4
5	0·722	30·9
6	0·984	36·6
7	1·438	47·2
8	1·835	54·5
10	2·869	68·7

The numbers in common use are 5 to 8. In 1914 the U.S. Institute of Makers of Explosives recommended the elimination of the manufacture and sale of detonators weaker than No. 6.[2] In Germany detonators weaker than No. 8 may not be used for ammonium nitrate explosives; in England No. 7 or 8 is used with these explosives.

Composition of Charge.

As regards the composition of the charge, in France fulminate of mercury only is used, but in other countries it is generally mixed with chlorate of potash up to 25 per cent. The total energy is thereby increased, as the carbon is converted into dioxide instead of monoxide:

$$Hg(CNO)_2 = Hg + N_2 + 2CO$$
$$3Hg(CNO)_2 + 2KClO_3 = 3Hg + 3N_2 + 6CO_2 + 2KCl.$$

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[1] C. G. Storm and W. C. Cope, *U.S. Bureau of Mines Technical Paper*, No. 125.

[2] *U.S. Bureau of Mines Bulletin*, No. 80, p. 36.

The theoretical proportion for complete oxidation is 77·7 of fulminate to 22·3 of chlorate: in practice 10 to 20 per cent. of chlorate is generally used. A further advantage of the addition of the chlorate is that it causes the charge to run better in the loading machines and bind together when pressed. Storm and Cope [1] found that the substitution of potassium chlorate for fulminate up to at least 20 per cent. increased the effectiveness of the detonators. By the sand test, detonators charged with the 80/20 mixture gave slightly better results than the 90/10 mixture, and pure fulminate somewhat worse. When small quantities were heated in test tubes larger weights of unmixed fulminate were required to fracture the tubes. The following were the numbers of tubes broken in 10 trials of each:

Weight of charge	0·04	0·05	0·06 grammes.
Fulminate	—	2	5
90/10 mixture	0	7	9
80/20 mixture	2	9	—

The following priming charges were required to detonate tetryl, tetranitroaniline and picric acid respectively, charges of 0·4 gramme being used and only lightly compressed:

	Tetryl	Tetranitro-aniline	Picric acid
Fulminate	0·35 g.	0·45 g.	0·40 g.
90/10 mixture	0·30 g.	0·312 g.	0·375 g.
80/20 mixture	0·275 g.	0·312 g.	0·375 g.

When compressed at 200 atmospheres and confined by a reinforcing cap the quantities required were:

	Tetryl	Tetranitro-aniline	Picric acid	Trotyl
Fulminate	0·22 g.	0·20 g.	0·25 g.	0·26 g.
90/10 mixture	—	0·17 g.	0·23 g.	0·25 g.
80/20 mixture	—	0·17 g.	0·22 g.	0·24 g.

The addition of potassium chlorate, however, makes the mixture slightly more hygroscopic and more liable to deteriorate. In some works the fulminate is pulverized by grinding it wet with a wooden pestle. By this the mechanical sensitiveness is decreased and the acceleration is increased, and so a double advantage is obtained, but the grinding operation is a troublesome and somewhat dangerous one.

Composite Detonators.

Detonators with composite charges are made up so that they shall be as strong as those of the corresponding number containing only a mixture of fulminate and chlorate. The following are some of the composite charges that are in use:

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[1] *U.S. Bureau of Mines Technical Paper*, No. 125.

No.	Trotyl or Tetryl	Fulminate of mercury
5	0·3 g.	0·3 g.
6	0·4 g.	0·4 g.
7	0·75 g.	0·5 g.
8	0·9 g.	0·5 g.

Some commercial trotyl detonators examined by Storm and Cope were found to contain the following quantities:[1]

No.	Trotyl	90/10 mixture
5	0·301 g.	0·312 g.
6	0·387 g.	0·316 g.
7	0·794 g.	0·314 g.
8	0·911 g.	0·338 g.

In the sand test they were found to give results equal to those given by fulminate detonators of the same grades. But they were more affected by moisture: after exposure for three days over water, during which 0·0039 g. of moisture had been absorbed by each detonator, the detonation of the trotyl was incomplete, whereas No. 7 detonators charged only with 90/10 mixture were still quite efficient after six days, during which they had absorbed 0·110 g. of moisture each. It was suggested that the priming charge of 0·31 g. was not sufficient to ensure detonation under adverse conditions of moisture.

The priming charge of fulminate receives extra confinement by being contained in a copper capsule or "reinforcing cap," which fits well inside the detonator tube and has in its base a small perforation to allow of the ignition of the fulminate. This capsule is pressed down on to the fulminate. For detonating insensitive explosives, such as trotyl of high density, detonators of special strength containing 2 grammes of tetryl are made.

Detonators have also been made charged with lead azide. These are very effective, but difficulties have been experienced in the manufacture.

For use with detonating fuse special detonators are made open at both ends. Into one end the safety or electric fuse is inserted and into the other the detonating fuse.

Boosters.

Recently brass tubes 4 inches long containing a charge of trinitro-toluene have been introduced under the name of renforts or boosters. They are made of such a diameter that they slip easily over the detonators. They are intended for use with gelatinized nitro-glycerine explosives to increase the

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[1] *U.S. Bureau of Mines Technical Paper*, No. 125, p. 59. *See also* Lheure, *P. et S.*, vol. xii., p. 134.

velocity of detonation.[1] A priming cartridge of a high explosive easy to detonate, such as dynamite No. 1, may be used for the same purpose.

Detonation of H.E. shell. In the case of high explosive shell there are special difficulties to be contended with. On the one hand the high explosives are necessarily insensitive, and on the other the arrangements for detonating them must be so designed that there is no danger of a premature explosion. For shell charges with picric acid use has been made of a comparatively large "exploder" or priming charge of picric powder, a mixture of ammonium picrate and saltpetre. The fuse of the shell ignites a charge of black powder, and this in turn ignites the picric powder which explodes with gradually increasing violence as the explosion extends, until it is sufficient to detonate the picric acid. For trotyl and other explosives of similar insensitiveness this arrangement is not sufficient to ensure detonation of a high order, and use has been made of intermediate priming charges of other high explosives which are comparatively easy to detonate. Trotyl in powder form or compressed under low pressure into pellets is sometimes used, but more usually tetryl which is more sensitive but is yet sufficiently safe. To detonate this priming charge a fulminate detonator is generally required, but this must be so mounted that there is no danger of its being fired by the shock of discharge of the gun. On the Continent quite large charges of fulminate have been introduced into shell, but this is not necessary if the shell be well designed. This is indeed one of the chief uses of tetryl, which is now manufactured on a large scale in all the principal countries of the world. In Spain tetryl was used for this purpose in February, 1907,[2] and in Germany considerably before then.

Precautions. In spite of every care explosions occur from time to time with such sensitive substances as fulminate, and in order to prevent widespread disaster it is necessary to restrict the quantities that may be present in any one place, and to separate the different working places and operations, so that an explosion at one spot may not cause other explosions. The German regulations lay down the following limits:

	Limit of explosive
1. Drying house and magazine for dry mixture	
(*a*) With a minimum distance of 10 m.	50 kg.
(*b*) " " " 15 m.	75 "
(*c*) Vacuum drying oven	0·5 "
2. Charge in press for wet mercury fulminate and wet composition	3 "
3. Mixing, corning, or sifting house for dry composition	10 "
4. Charge of the mixing, corning, or sifting appliances for dry composition	5 "
5. Charging compartment for detonators	1 "
6. Charging compartment for percussion caps	
(*a*) Machine charging with loading machine separate	500 g
(*b*) " " with loading machine not separate	100 "

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[1] *Bureau of Mines Bulletin*, No. 80, p. 35.

[2] *See* R. Aranaz, *Memorial de Artilleria*, April, 1908; S.S., 1908, p. 309.

	Limit of explosive.	
(*c*) Hand charging with separate filling room	100	g.
(*d*) ,, ,, without separate filling room	30	,,
(*e*) ,, ,, protected with shield	500	,,
(*f*) Contents of transport case	1500	,,
7. Store for detonators	1000	kg.
8. Concrete magazine for detonators	3000	,,

The greatest care should be taken not only to remove from the range of possible explosion any composition or finished caps or detonators not actually required for the work in hand, but also to clean up at frequent intervals any composition that may be spilt or blown about. Accidents have been caused by workpeople treading on spilt composition or detonators.

Disposal of waste.

The disposal of waste composition and articles containing it is a matter of importance and some difficulty. The German regulations lay down that mother liquors from the fulminate, as well as all wash waters and residues, must be deprived of their explosibility before they are run to waste. It is recommended that this be done by boiling the strongly acid liquid for four or five hours in vessels of earthenware or wood by means of steam-coils or live steam. Alkali or sodium sulphide should not be added, as it is liable to lead to the formation of dangerous intermediate compounds. Moistened waste composition may be destroyed in the same way, or it may be stirred with a mixture of 3 parts of hydrochloric acid and 1 part of nitric acid until the fulminate of mercury has been entirely destroyed. When the vessel is emptied, the solid residue should be collected on a filter cloth, or the liquid should be drawn off by means of a cock so placed that only liquid can escape by it. The liquid should be neutralized with lime before it is run to waste. The solid residue should be tested as to its explosibility, and the boiling should be continued until it is inexplosive.

Filter cloths, sponges, etc., should be kept under water and put into a fire whilst still wet. Sawdust, which has been in contact with composition, should be destroyed in the same way.

Waste detonators and caps are to be kept in sawdust and destroyed by burning at least once a week. In the case of detonators, the burning place should be protected.

The English Inspectors of Explosives, on the other hand, recommend that detonators be destroyed by dissolving them entirely in a mixture of 2 parts concentrated hydrochloric acid and 1 part water.

Loose composition or fulminate can be destroyed very rapidly by stirring it with a solution of sodium thiosulphate in excess, but the liquid should be kept slightly acid by the addition of sulphuric acid. Large accumulations of explosive waste should be avoided.

Vennin states that fulminate can be destroyed by means of a solution of ferrous sulphate,[1] but I have found this method to be ineffective.

If large numbers of waste detonators have to be destroyed, they may be tied together in bundles of 50 or 100 with an electric detonator in the middle, and the whole bundle can be detonated at one time. The explosion should be carried out in a suitable pit, and the men should be properly protected.

Testing detonators.

The strengths of detonators can be compared by firing them in contact with lead plates, on which they are either laid or stood vertically.[2] The violence of the detonator is judged not only from the size of the depression or hole made, but even more from the number and depth of the striations on the surface of the lead made by the minute particles of copper from the capsule. Or they may be detonated in small lead blocks similar to those used for the Trauzl test but smaller. This, however, is not very satisfactory, as it determines the power of the detonator and not the brisance, which is much more important. A better method is to ascertain their power of detonating an insensitive explosive: by means of the Trauzl test or by determining its velocity of detonation it is possible to make certain whether the detonation has been complete.

Nail test.

The U.S. Bureau of Mines has adopted a test in which the effect of the detonator on a 4-inch wire nail is measured:[3] the detonator is attached to the nail so that the bottom end is $1\frac{3}{4}$ inches from the face of the head of the nail (see Fig. 111). The nail and the detonator are parallel to one another and separated from one another by two 22-gauge (0·025 inch) copper wires that are wrapped round the detonator. The nail is fastened to the detonator by a single strand of the same wire round the middle of the detonator. When the detonator is fired the nail is bent and projected upwards: the angle to which it is bent is a measure of the strength of the detonator. The nails should, of course, be uniform in quality and dimensions. Fig. 112 shows the effects produced by detonators Nos. 3, 4, 5, 6, 7 and 8.

Sand test.

In another test, worked out by C. G. Storm and W. C. Cope of the U.S. Bureau of Mines, the detonator is immersed in standard sand, and the quantity of fine powder produced on firing it is ascertained.[4] Practically pure quartz sand is used which passes entirely through a 20-mesh sieve and is held by a 30-mesh. Of this 100 grammes are taken and placed in a chamber 15 cm. deep and 3·1 cm. in diameter bored out of a steel block covered with a strong lid. In the centre of the sand the detonator is placed and fired. Then the sand is sifted through a 30-mesh sieve and the quantity of fine sand that

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[1] Vennin et Chesneau, p. 291.

[2] *See* Fig. 102.

[3] *See U.S. Bureau of Mines Bulletin*, No. 59: "Investigations of Detonators and Electric Detonators." Also *Bulletin* No. 80, p. 41.

[4] *Bureau of Mines Technical Paper*, No. 125. *See also* G. B. Taylor, and W. C. Cope, *Technical Paper*, No. 145.

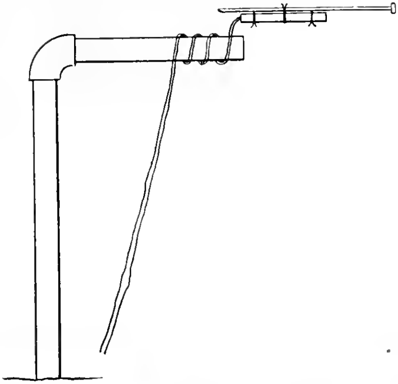

FIG. 111. Nail Test for Detonators

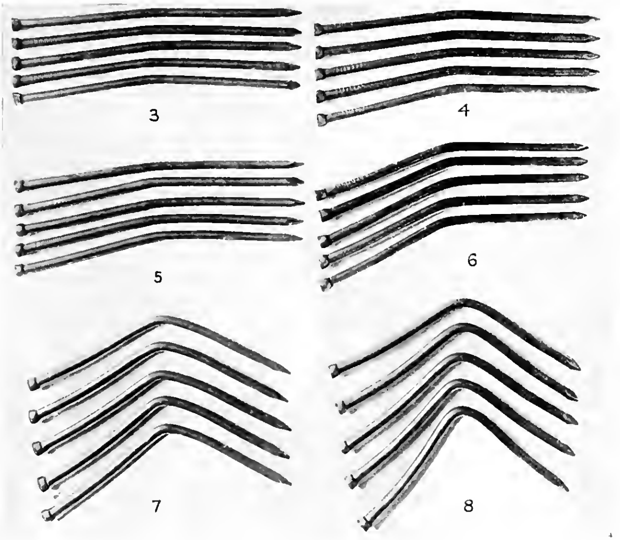

FIG. 112. Nail Test for Detonators

passes through is taken as a measure of the effectiveness of the detonator.

Esop's test. K. Esop devised a method for measuring the strength of detonators, which consisted in taking a suitable explosive, such as picric acid and mixing with it cotton seed oil until he found what percentage could be added without preventing its detonation by the detonators under test.[1] He found that this percentage could be determined within very close limits. The picric acid, which must be uniform in grain, is mixed thoroughly with the oil and is then compressed to a cartridge of certain standard dimensions. The detonator is inserted in the cartridge, which is then placed on the upper one of two steel plates, which in turn rest on two lead cylinders. From the compression of the lead cylinders it is judged whether detonation has occurred. The following results were obtained:

Oil added to 50 g. picric acid	Compression	
0	25·4 cm.	
1·56 g.	25·1 cm.	
1·58 g.	23·9 cm.	
1·60 g.	24·7 cm.	
1·62 g.	2·2 cm.	These small compressions are due to the detonators alone.
1·68 g.	2·1 cm.	

No independent evidence as to the value of this ingenious test appears to have been published.

Sound tests. F. Martin compares the brisance of detonators by observing their effects on sensitive flames.[2] This is, of course, really a comparison of the amount of noise they make. Other proposals have been made to measure the intensity of the sound by means of a microphone and sensitive galvanometer. The weak point of these methods is that there is no necessary connexion between the intensity of sound and the efficiency of the detonator. A feeble explosion giving rise to a secondary explosion of the gaseous products with air always makes a great noise.

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[1] *Mittheilungen über Gegenstände des Artillerie und Geniewesens.* 1889.

[2] *Chem. Zeit.*, vol. xxxvii., 1913, p. 90.

PART X

SOME SPECIAL EXPLOSIVES, ETC.

CHAPTER XXXII

FUSES

Safety fuse : Igniter fuse : Miner's squibs : Quills, etc. : Quick-match : Instantaneous fuse : Slow-match : Detonating fuses : Electric fuses : Electric igniters : Mechanical fuses : Shell fuses : Initiation by stages

For the ignition of the detonator or, in the case of blasting explosives of the black powder class, for the direct ignition of the charge, a fuse of one sort or another is used. This is a device by which a flame is communicated to the detonator or charge either after an interval of time, or by an operation conducted at a distance. In either case the shot firer is not exposed to the effects of the explosion.

Safety fuse.

Safety fuse is made or "spun" by allowing fine grain black powder to flow down from a hopper into an inverted cone, in the apex of which there is a small hole. Down the outside of this cone some ten threads, usually of jute, are drawn from reels, through holes drilled in the flange at the base. Below and just clear of the apex of the cone is a thick metal disc, through which the threads pass with the stream of powder in the middle. Then the whole cord passes through a tightening tube. At the same time the frame supporting the reels is rotated so that the thin column of powder is enclosed in a spiral tube. Lower down in the same machine is another similar frame supporting other reels, usually seven in number, and this is rotated in the opposite direction, so that the fuse is doubly wound or "countered." The fuse is then wound on to a drum, on which it is transported to other buildings, where it undergoes further operations, such as winding with tape and impregnating with waterproofing material. The spinning operation must be carried out with the usual precautions required in manufacturing operations with explosives. The floors must be kept clean, and the operatives, usually girls, must wear special clothing without pockets. The hoppers containing the powder should be situated in a loft above the actual spinning-room, so that in the event of an ignition the workers have time to escape before the powder explodes.[1] For descriptions and illustrations of some of the machinery used in the various operations of manufacture, *see* Neumann, *S.S.*, 1910, pp. 87, 107, 130, 148, and 168.

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[1] *See S.R.*, Nos. 140 and 178.

A great many varieties of safety fuse are made, differing principally in the number and character of the layers of covering material, and in the waterproofing applied, if any. In England it is sold in coils of 24 feet, but in America they are 25 or 50 feet long,[1] and on the Continent 10 metres (about 33 feet). In Germany the fuse is coloured to distinguish the different manufacturers one from another, but in England a further distinction is made by varying the colouring of the different varieties.

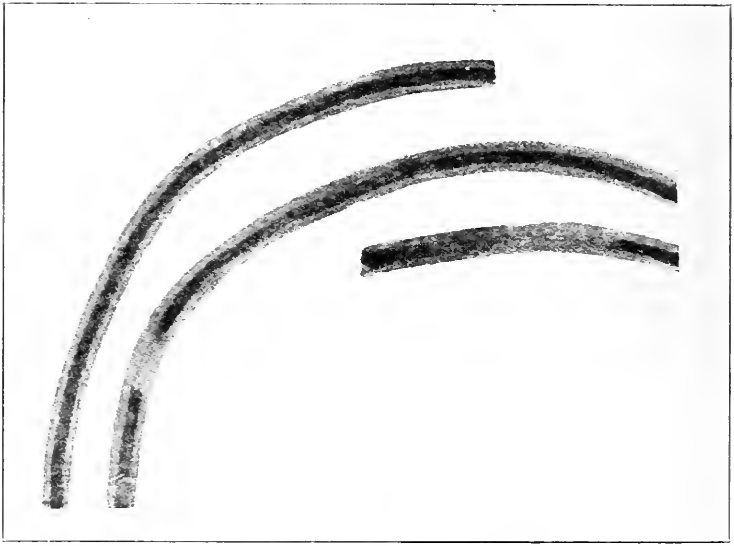

Fig. 113. Safety Fuse under X-rays

Rate of burning.

Regularity in burning is the first requisite of safety fuse: usually it is made to burn in the open at the rate of about 30 seconds per foot or 100 seconds per metre. Sometimes a fuse will fail altogether on account of an interruption of the powder core. Hake pointed out [2] that such interruptions can be detected by examining the fuse under the X-rays (*see* Fig. 113). The rate of burning is usually measured in the open, but unfortunately it is much affected by the

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[1] For different varieties of American safety fuses *see* *U.S. Bureau of Mines Bulletin*, No. 80, p. 30. In America this fuse is also called burning or running fuse.

[2] *J. Soc. Chem. Ind.*, 1903, p. 1224.

pressure to which the fuse is subjected: if tamped hard with plastic clay the rate of burning may be increased to three or even five times the normal rate;[1] with porous and less plastic tamping materials, such as dry clay or sand, the powder gases can escape as they are formed, and the rate of burning is only slightly increased. Snelling and Cope[2] found that under an air pressure of one atmosphere the rate of burning was increased about 30 per cent. Exposure to a high temperature makes the fuse burn more slowly, especially if it be coated with waterproofing material which becomes soft under this treatment. If stored for a long time in a damp place, the burning is retarded and may be interrupted altogether.

Waterproof fuse must be capable of burning properly after a longer or shorter immersion in water, and colliery fuse must not give off laterally any sparks that could ignite coal-damp. The following are the tests applied officially to fuse imported into or stored in South Africa:[3]

(*a*) The fuse may be opened and the various materials examined to ascertain that they are of good quality.

(*b*) All safety fuse shall burn between the limits of 90 seconds and 110 seconds per yard, and must burn uniformly throughout its length.

(*c*) A piece of fuse 4 yards long shall be immersed in water, except for 6 inches at either end, for a period of 12 hours, at the end of which time it must burn through as in (*b*).

(*d*) A piece of fuse 2 yards long will be folded up four times and thrust into a piece of iron piping 1½ inches in diameter and burnt both in the open and under water: the former to test for lateral communication, the latter to test for waterproofing.

(*e*) The flash from the end of a piece of fuse shall be such as to ignite another piece of fuse at a distance of 1 inch. (For the purpose of this test a short length of fuse will be inserted into either end of a piece of glass tubing and one end will be ignited. The flash must ignite the other piece of fuse.)

Igniter fuse.

In fiery coal-mines the use of a naked flame to ignite the safety fuse would be dangerous. Consequently devices are made for lighting the fuse in a closed space. The third schedule of the Explosives in Coal-Mines Order of May 21, 1912, lays down that: "The fuse shall consist of a core of gunpowder, protected by not less than three coverings of thread or by not less than two coverings of thread and one of tape or gutta-percha. The fuse shall be of such quality that the time of burning of the fuse shall not vary more than 10 seconds above or below the rate of 90 seconds for every yard of fuse. The fuse shall be ignited by means of an igniter contained in a tube which when attached to the fuse forms a completely closed chamber." In the second schedule of the Order of February 21, 1910, the following description is given

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[1] *See S.S.*, 1908, p. 348.

[2] *Bureau of Mines Technical Paper* 6, Washington, 1912.

[3] *South African Explosives Act*, 1911, p. 45.

of Bickford's Igniter Fuse: "... consisting of a tube of tinned iron or steel, closed at one end, and containing a mixture of chlorate of potassium and sugar pressed into a pellet not exceeding 100 milligrammes in weight, in close contact with a hermetically sealed glass capsule containing concentrated sulphuric acid: a length of specially prepared colliery fuse, as is hereinafter defined, being fitted into the open end of the tube and the joint being cemented by a tape bearing the 'Crown' and letter 'P.' . . .

"The said fuse shall consist of a core of gunpowder in weight not exceeding 6 grammes per metre, traversed by two threads and enclosed by:

"(1) A layer of jute yarn: (2) a layer of jute yarn laid in the contrary direction: (3) a layer of tape: (4) a layer of tape laid in the contrary direction; (5) a layer of jute yarn secured by a suitable varnish. (The three outer layers being specially treated with a fireproofing composition.)"

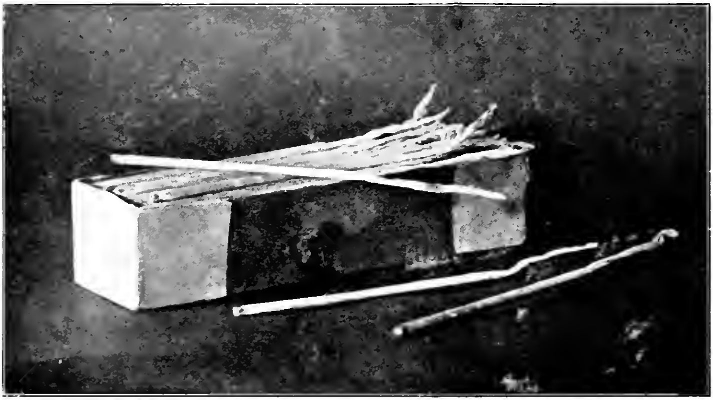

FIG. 114. Miners' Squibs
(From *Bureau of Mines Bulletin*, No. 17)

For fireproofing, such substances as ammonium phosphate and sodium tungstate may be used. For fuse of this sort jute or hemp is better than cotton, because it is less liable to smoulder.

The special tests to which igniter fuse is subjected were laid down in *A.R.*, 1906, Appendix O, p. 143:

(1) Five lengths of 12 inches of the fuse to be ignited. This must show no visible incandescence anywhere even when fanned.

(2) Five lengths of 12 feet of the fuse with the lighters attached to be

wound round a 2-inch cylinder, straightened, and fired by means of the recognized firing arrangement, the whole, except not more than 6 inches of the cut end, being in a highly explosive atmosphere of coal-gas and air.

(3) Test No. 2 to be repeated with twenty igniters and shorter lengths of fuse not previously wound round a cylinder, to test lighting arrangement only.

The fuse is considered to have failed if it causes an ignition in either 2 or 3.

This igniter fuse is practically the same as the Colliery Safety Igniters, which have been in use to some extent for many years. The same idea has been put forward by Roth and also by Zschokke.[1] Proposals have also been made to ignite the safety fuse by some frictional device. A. F. Hargreaves, for instance, patented the idea of igniting a fuzee with sandpaper inside a cover.[2]

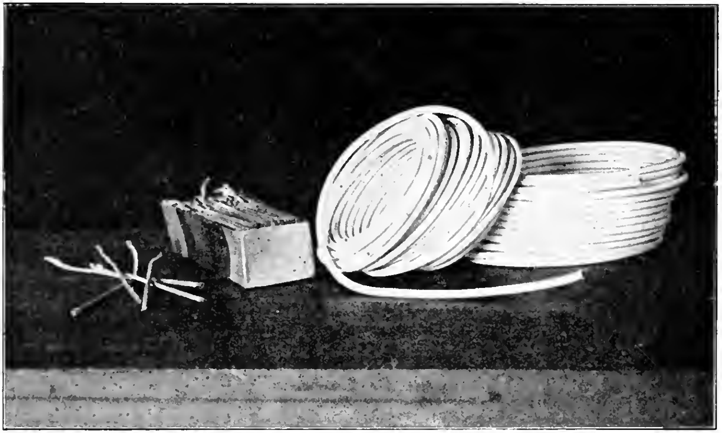

FIG. 115. Squibs and Safety Fuse

Miner's squib.

More primitive igniting arrangements are still used in some mines and quarries, where stringent regulations are not in force. One device is the miner's squib (Fig. 115), which consists of a tapering paper tube about 7 inches long, filled with fine gunpowder. One end of the paper tube is treated with chemicals so as to form a slow-match, which when ignited takes so long to burn that the miner has time to reach a place of safety before the explosion. When used, the squib is placed in the needle hole or blasting barrel through

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[1] *See Cundill and Thomson's Dictionary*, p. 29.

[2] Brit. Pat. 13,880 of June 15, 1907. *See also* Vennin et Chesneau, p. 470.

the tamping with the match end of the squib outward. When the match is lit, the fire burns slowly until it reaches the powder core; then the squib darts forward like a rocket, leaving a trail of flame behind, which spurts out of the needle hole, and the fire continues burning along the squib until it bursts out at the other end of the tube and so ignites the charge. This invention was patented in 1874 by Daddow [1] and has been used largely in the Cleveland iron district. Miners' squibs are practically identical with Hunter's mining fuses and German spills.

Quills, etc. Another simple device is a quill filled with powder and joined to a piece of slow-match. Strips of blasting gelatine are also used. These are all very objectionable and dangerous. In South Africa "Cheesa sticks" are used, which consist of sticks of cordite coated with ammonium oxalate and shellac. They have recently been authorized in England.

Quick-match. Quick-match was formerly used for igniting charges both in military and civil blasting: it is still used in making up fireworks, etc. It is made of cotton wick boiled with a solution of mealed powder and gum, and afterwards, before it is quite dry, dusted over with mealed powder. It may also be made by soaking cotton thread in an alcoholic solution of gum and then dipping it into gunpowder.[2] Unenclosed it burns at the rate of a foot in about four seconds, but if enclosed in a tube it burns much more rapidly.

Instantaneous fuse. Instantaneous fuse consists of several strands of quick match enclosed in a wrapping of waterproof tape: its speed is from 100 to 300 feet per second. Formerly it was much used in extensive blasting operations, where a number of charges had to be fired simultaneously, but it has now been superseded by electric detonators and detonating fuses. It was fired by means of a percussion cap in a special pistol.

Slow-match. Slow-match is made by boiling loose hemp cords in a dilute solution of saltpetre; it smoulders away at the rate of a foot in several hours; it is used when a long delay is required.

Detonating fuses. Many attempts have been made to produce a fuse more rapid than instantaneous fuse by filling it with an explosive capable of being detonated, but it is only of recent years that real success has been achieved. As long ago as 1879 a detonating fuse was introduced into the French army: it was made by filling a lead tube with pulverulent nitro-hydro-cellulose and then drawing it out until it had a diameter of 4 mm. A metre weighed about 88 g. and contained 5 g. of the gun-cotton; it detonated at the rate of about 4000 metres per second. It was somewhat sensitive to blows, and does not seem ever to have come into general use. Attempts to make detonating fuse filled similarly with other powdered explosives were also unsuccessful. In Austria General Hess introduced a fuse constructed on the same principles as instan-

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[1] Brit. Pat. 1558 of May 2, 1874.

[2] *See S.S.*, 1915, p. 273.

taneous fuse, except that the threads were impregnated with a mixture or paste of fulminate of mercury, glycerine and water, but more recently the fulminate has been phlegmatized with 20 per cent. of hard paraffin instead. The fuse thus produced (Knallzündschnur M.03) is stated to be satisfactory.[1] Only a very violent blow will cause it to explode; if ignited, it merely burns away, but if heated so much that the paraffin melts and separates from the fulminate, it becomes dangerous. When fired with a 2 g. detonator it detonates at the rate of 5000 to 6000 metres per second.

In Italy fuse has been made by filling a lead tube with finely powdered ballistite. It can be used either as a detonating or slow-burning fuse. In order to enable it to burn under water some black powder is mixed with the ballistite. In spite of statements to the contrary, this fuse must deteriorate rapidly on keeping.[2] When fired with a 1 g. detonator it detonates at the rate of 5000 metres per second; when lit, a metre burns in four minutes.

In France detonating fuse has been made by filling tin tubing with powdered picric acid, and then drawing it out. A great improvement was effected by Lheure, who for this substituted trinitro-toluene in a lead pipe. The explosive is melted and drawn into the lead tube by vacuum, and when cold the tube is drawn out to a diameter of about 4 mm., using special precautions to ensure uniformity. Other explosives, which are insensitive, easily melted and not plastic, can be used, such as tetranitro-methyl-aniline or trinitro-benzene, but they are more expensive. Trinitro-toluene is therefore used by the manufacturers, Davey, Bickford, Smith et Cie., of Rouen. This fuse has been used successfully for some considerable operations, such as the destruction of a canal tunnel at Hollebeek in Belgium, where 2125 charges were fired simultaneously, amounting to 3250 kg. of explosive. The principal use of detonating fuse is for military demolitions, in which the simultaneous explosion of a number of charges is of importance, as also are simplicity and ease of application. For some purposes, such as the destruction of iron fences, the fuse can be used by itself. For use in ordinary mines and quarries its high price is somewhat prohibitive, but it is contended by Lheure[3] that it can be used in coal-mines without increasing the danger, and that its use leads to a saving of 20 per cent. of the explosive (grisounite). The saving is apparently due to this very insensitive explosive not being detonated entirely by an ordinary detonator, whereas with a piece of detonating fuse running the whole length of the charge detonation was complete, or at any rate more nearly so. For the detonation of insensitive explosives, Brunswig[4] advocates that advantage should be taken of the fact that at the point where two waves of detonation meet in a piece of fuse detonated from both ends, the effect is

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[1] *See S.S.*, 1907, p. 173.

[2] *See* Neumann, *S.S.*, 1910, p. 172.

[3] *Annales des Mines*, 1907: *S.S.*, 1908, p. 141.

[4] *Eighth Inter. Cong. App. Chem.*, 1912, vol. iv., p. 23.

very much greater, a closed loop of detonating fuse being immersed in the cartridge. This fuse is utilized for the measurement of the velocity of detonation of explosives.

Some detonating fuse examined by the United States Bureau of Mines [1] had an external diameter of 0·1645 inch (4·18 mm.) and internal diameter 0·1145 inch (2·91 mm.). The charge was very finely powdered, soft and slightly cohesive. It had a density of 1·32. Bichel on the other hand gives the density as 1·5. The fuse is also made with a diameter of 5 mm.

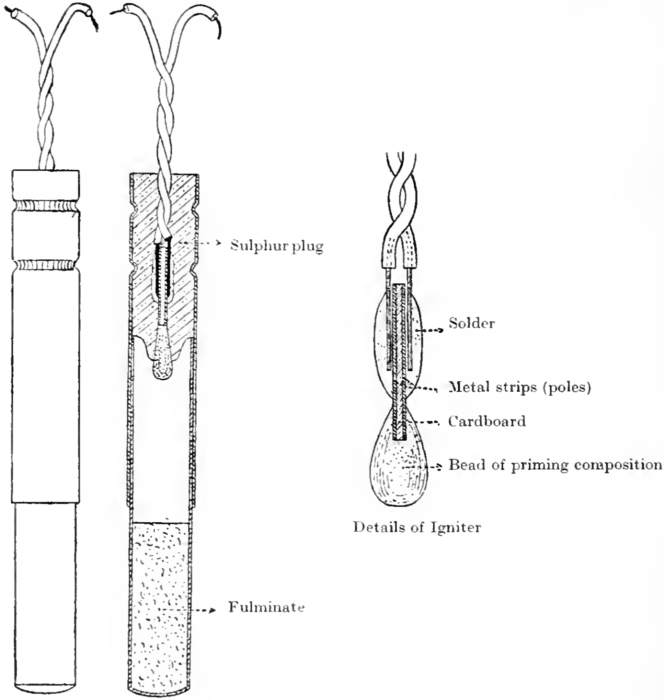

Fig. 116. Electric Detonator

Another French firm makes flattened tubes filled with tetranitro-methyl-

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[1] *Bulletin* No. 80, p. 35.

aniline, and for work in coal-mines, with this substance mixed with nitroguanidine.[1]

Electric fuses.

The development of electrical science and industry naturally led to the idea of firing explosives by means of an electric current. Heat generated by a current is utilized to fire a suitably constructed fuse, and this ignites a detonator, which in turn explodes the charge. Much ingenuity has been devoted to the designing of electric fuses, but they may be divided into two main classes: high and low tension fuses. In the former a spark is made to pass between two metal poles and ignite a priming material such as a tuft of gun-cotton, or a mixture of potassium chlorate and antimony sulphide. In the low-tension fuses there is a small bridge of fine wire, generally made of platinum, and this is heated to incandescence by the current, thereby igniting the priming. The fuses now used are nearly always of the low-tension type: one of the advantages that they possess over the other type is that each fuse before use can be tested as to the resistance that it offers to the current, whereas a high tension fuse can only be tested by firing, and so destroying it. When testing the resistance of a detonator it should always be inserted in a safety receptacle so that if it should fire, no harm will be done.[2]

In order to protect the fine wire bridge from fracture it is often embedded in a solid bead of priming composition. As a rule the electric primers are attached to the detonators in the factory, and the electric detonators thus made are supplied complete ready for firing. Fig. 116 shows, for instance, the construction of the electric detonators made by the "Fabrik Elektrischer Zünder," in Cologne. The two connecting wires are soldered to two strips of metal foil, which are attached to the opposite sides of a piece of cardboard. For low-tension fuses these strips are connected by a piece of platinum wire, and the whole is dipped into a mixture containing potassium chlorate and antimony sulphide, so as to form a bead like the head of a match, which is then further protected with a covering of shellac and collodion. This is fixed into a tube by means of a plug of molten sulphur, and this tube is slipped over the open end of the detonator capsule, to which it is attached by means of shellac cement. A typical American electric detonator is shown in Fig. 117.

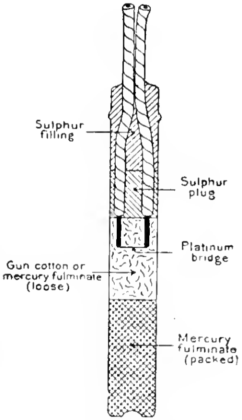

Fig. 117. Electric Detonator

(From *U.S. Bureau of Mines Bulletin*, No. 80)

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[1] *See* Chalon, *Explosifs modernes*, 1911, pp. 424–428.

[2] *A.R.*, 1910, p. 30.

The wires should not, however, be in contact with very sensitive explosives, such as fulminate, because there is always danger that they may move when handled, and so cause a premature explosion.

The advantages of the electric detonators are that they can be fired from any distance at any moment, and that a number of shots can be fired simultaneously. In blasting a round of holes in hard rock, it is often desired to explode some of the charges before others. This can be done by causing a delay in the firing of the electric detonators for the later shots, as, for instance, by introducing a piece of safety fuse between the electric fuse and the detonator. Delay electric detonators are also made in which the whole arrangement is supplied complete. Electric firing suffers under the disadvantage that it is considerably more expensive than firing with safety fuse, but from an analysis of the results obtained during several years in the coal-mine of Heinitz on the Saar, Bulgis finds that though the cost per shot is higher, per ton of coal got it is lower, with electric firing:

		Average cost	
		Per ton coal	Per shot
Safety fuse . . .	1907	0·30*d.*	1·02*d.*
	1908	0·28*d.*	0·92*d.*
Electric . . .	1908	0·28*d.*	1·38*d.*
	1909	0·24*d.*	1·38*d.*

The saving is ascribed to the fact that the electric firing is carried out by special shot-firers, whereas the firing with safety fuse was done by the miners themselves. The miner is inclined to reduce the number of shots to be fired to minimum in consequence of the trouble and annoyance of having to wait for the shot firer to come round.[1] Electric detonators only are allowed to be used in French coal-mines.[2]

Electric fuses are generally made with a resistance of about 1 ohm, and fire with a current of about 0·7 ampère. A few shots can be fired simultaneously by means of a portable battery, but for large numbers this will not give a sufficiently powerful current. They are generally connected up in series with an "exploder," as is shown diagrammatically in Fig. 118. The usual type of exploder consists of a small compound series wound dynamo worked by hand by means of a rod which is pushed down. The voltage is built up

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[1] *S.S.*, 1908, p. 361; 1909, p. 41; 1911, pp. 192 and 352.

[2] Vennin et Chesneau, p. 131.

rapidly during the stroke until the rod nearly reaches the end of its stroke, when the current is switched into the circuit and fires the shots. Such exploders may be obtained guaranteed to fire 50 or 100 shots simultaneously, but it has been found in the operations on the Panama Canal that there are always some missfires, due to the fact that some of the fuses are more sensitive than others, and they detonate and so destroy the circuit before the less sensitive ones have reached the exploding point.[1] Recourse was therefore had to firing all shots in parallel through a transformer from the main electric supply, and so all trouble from this source was overcome. The reason why there were more failures at Panama, than in ordinary blasting operations, was that very large charges were used at considerable distances apart: holes were drilled to depths of 15 to 60 feet, 12 to 18 feet apart, and each was charged with from 200 to 1000 lb. of dynamite. In ordinary blasting operations the holes are only a few feet apart, and under these conditions, if a detonator fails, the charge is exploded by influence from the other charges and consequently the danger from unexploded charges is much less; but the effect of the charges fired by influence is comparatively small.

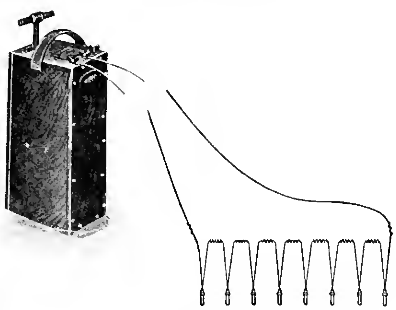

FIG. 118. Electric Exploder and Detonators (Du Pont)

There are also electric fuses specially made to overcome this difficulty by short circuiting the connecting-wires when they are fired. The circuit consequently is not broken at once, but for a small fraction of a second there is an extra powerful current available for firing the less sensitive fuses.[2]

Another defect, that was found to cause failures at Panama, was that the electric detonators were not always quite water-tight, with the result that after immersion in a deep bore-hole for some hours they failed. The failures were traced to the action of the sulphur plug on the copper of the shell, whereby the latter was made porous. The detonators in question were of American manufacture.

Electric igniters.

For firing charges of explosives of the gunpowder type, electric igniters can be used similar in construction to electric detonators, except that the

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[1] *See* Robinson, *Eighth Inter. Cong. App. Chem.*, 1912, vol. iv., p. 85.

[2] *See S.S.*, 1912, p. 459.

capsules are made of paper or wood instead of copper, and are charged with a gunpowder mixture of fulminate.

Mechanical fuses.

Fuses can also be made that are fired by mechanical action as, for instance, by pulling a wire or cord, which releases a striker which is driven by a spring on to a percussion cap. Such devices are but little used, however, except for fuses for firing artillery shell.

Shell-fuses.

There are two main varieties of fuses for shell, namely, percussion and time fuses. The former may be fixed into either the base or the nose of the shell: in either case they generally work on the same simple principle: when the shell strikes an object the sudden retardation either causes a pin to strike a percussion cap or makes the cap fall on to the pin. The flash from the cap ignites some priming composition, and so the ignition is communicated into the interior of the shell proper. The fuses may be provided with a delay arrangement, a small pellet of combustible matter, which must be burnt through before the flame can reach the shell. This causes the shell to explode only after it has travelled some distance through the armour plating of a ship, for instance. The fuse must, of course, be so constructed that the cap is not fired by the shock of discharge of the gun, nor by such blows as it may receive in handling and transport. The moving part is therefore held in place, usually by a spring, which can only be overcome by a very severe blow on the nose of the shell. In the case of shell filled with high explosive, the result of a premature detonation in the bore of the gun would be so disastrous, that special safety arrangements are generally introduced. The percussion cap is entirely cut off from the interior of the shell until some disc or bolt has been removed either by the pressure of the powder gases on the base of the shell, or by the centrifugal force caused by the rotation of the shell.[1]

Time fuses are used mostly for shrapnel shell, which is required to burst shortly before it reaches the object shot at. But, as a rule, the fuse also contains a percussion arrangement, so that, if the time mechanism does not function, the shell will still be exploded when it strikes, and so may be of assistance to the artilleryman in gauging the range, even if it does no damage. Time fuses are always fixed to the nose of the shell. The primitive fuses used in the early days were made to ignite by the flame of the powder charge, but now the concussion of the discharge is utilized to fire a percussion cap. Before the flame can reach the bursting charge it has to burn through a lengthy column of comparatively slow-burning composition, generally placed in one or more movable rings. The gunner by twisting one of these round can alter the length of the column to be burnt through, and consequently the range at which the shell will burst. The construction of time and percussion fuses is shown in Fig. 119. Each ring has a circular slot cut in it nearly all the way round; it is ignited at one end and the flame travels round until it comes

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[1] *See* Exler, *S.S.*, 1909, pp. 63 and 88.

to the hole leading to the next ring or to the priming. Formerly the rings were filled with mealed powder pressed into the slots, but now fine grain gunpowder is generally used, as its time of burning is more regular, a very important consideration. In Austria it is pressed to a density of 1·8 and corned in the usual way; the grains used measure 0·3 to 0·65 mm. This powder is pressed firmly into the rings.

The time of burning of a fuse with two rings having a total length of 20 cm. filled with gunpowder of the standard composition is about twenty seconds. The range of modern artillery is so great, however, that this is not sufficient in many cases. It is necessary to devise fuses which have a time of burning of some forty seconds without any increase in the relative variation in the time. Ten fuses, burnt under service conditions, should not show an extreme variation of more than 2·5 per cent. of the mean time. An increase in the

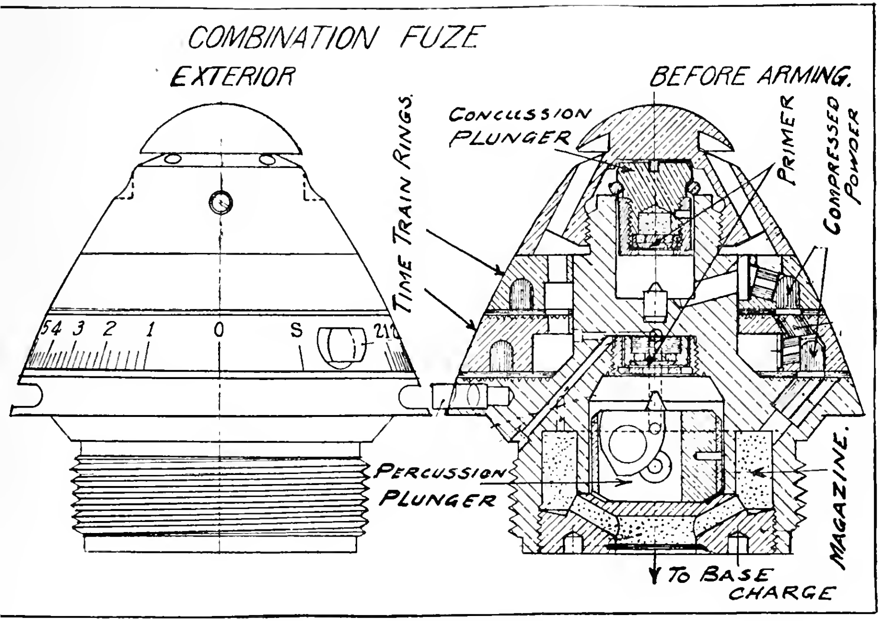

Fig. 119. Time and Percussion Fuse

(From Major O'Hern's paper in *Smithsonian Report*, 1914, pp. 249–275) number of rings adds to the complication and increases the cost, which is already considerable. The powder can be made somewhat slower by increasing the percentage of saltpetre or decreasing that of the charcoal.[1] The addition of graphite has a slight effect in the same direction, and also makes the powder more regular. The addition of vaseline and the substitution of barium nitrate for part of the saltpetre also lengthen the time of burning, but none of these changes makes the powder as slow as is required. The addition of non-volatile inert matter, such as steatite or brickdust, is not desirable, as it tends to block the passages through which the gases escape. The desired effect can, however, be produced by the use of very slack-burnt charcoal. Dolleczek found that when the yield of charcoal was about 50 per cent. of the wood used, the time of burning was a minimum, namely, about 15 seconds. With a yield of 71 per cent. the time was 25 seconds, and with 80 per cent. 37 seconds. The percentages of carbon in these charcoals were 68, 58, and about 55 per cent. respectively. A brown powder such as was formerly used for ordnance was also tried. The charcoal in this contained only 52 per cent. carbon. The powder by itself would not ignite in the time rings, but when mixed with black powder in various proportions and worked together the mixtures gave times of burning of 40·21 and 33·63 seconds with differences of 1·12 and 0·70 seconds respectively. Promising results were also obtained with slack burnt cork charcoal.

Shell fuses are generally constructed of brass. Aluminium is also used on account of its lightness, but gunpowder should not be placed in contact with this metal as it causes it to corrode. If the time rings are made of aluminium or aluminium alloy the composition channels should be lined with brass.[2]

One of the difficulties in the construction of time fuses is to make them sufficiently air-tight to prevent the absorption of moisture by the powder. A small increase in the percentage of water in the composition contained in the time rings makes them burn considerably more slowly, and if the composition takes up sufficient moisture to become really damp, the fuses become quite unreliable, even when they are dry again. The escape holes are protected with waterproof discs, and the edges of the time rings are coated with thick lubricant, but even so, care has to be taken in the storage and transport of the fuses in order to maintain them in a serviceable condition. Metal caps are frequently kept fixed over the fuse until it is actually required for use. This question has been dealt with somewhat fully by Gründlich.[3]

In France an entirely different solution of the difficulties connected with the construction of long-range time fuses has been worked out. The time composition, which is a mixture of pulvérin and gum lac, is filled into a lead tube,

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[1] *See* Dolleczek, *S.S.*, 1910, pp. 245 and 273.

[2] *See* Bethel, *Journ. Roy. Art.*, 1913, p. 301

[3] *S.S.*, 1911, pp. 221, 248, 270, and 291.

which is then drawn out by passing it through a number of draw plates until its diameter is reduced to a few millimetres. This tube, which burns very regularly, is wound in a spiral inside the fuse. To set the fuse, this tube is stabbed at the appropriate point, whereby the flame is caused to impinge on the priming at the proper time. The tube can, of course, be made of any desired length, and the composition is effectually protected from moisture.[1]

Many attempts have been made to design fuses in which the interval of time is measured off, not by the burning of a composition, but by some mechanical action, such as the passage of air or liquid through an orifice, or in which the space travelled through by the shell is automatically measured by a vane projecting from the nose, which after a certain number of revolutions fires the shell.[2] The only successful fuse of this sort, so far, is that invented by Bäker and taken over and perfected by Krupp, which has a clockwork mechanism driven by a spring. This has been described in detail by Neumann in *S.S.*, 1912, pp. 1 and 25. Unlike the time-ring fuse it is not affected by atmospheric pressure or length of storage, and it is claimed that it is more accurate. It has been stated[3] that the Germans are using it for their long-range artillery, but this statement needs confirmation.

Fuses are tested by jolting them in order to ascertain that they will withstand the rough usage of active service. But the most important test is to fire them in shell to see if they function properly. Time fuses are tested for time of burning whilst being spun, or when fired from the gun in a shell.

Initiation by stages.

The powder in a small-arm cartridge is fired directly by the flame from the cap, which is ignited by the blow of the striker upon it; but a cannon cartridge requires also to have an igniter of some easily fired explosive such as gunpowder, as the flame from a cap or tube is quite insufficient to ignite smokeless powder of large size with regularity.

For firing high explosives use is made of a detonator, which is fired by means of a fuse. Most commercial explosives are made to detonate with a detonator containing not more than 2 grammes of fulminate of mercury, but gelatinized nitro-glycerine explosives, such as blasting gelatine, are much more violent if a primer of an ungelatinized explosive, such as dynamite, be used as well. For many naval and military purposes much less sensitive explosives are required, and these can only be detonated with certainty by means of a priming of some other powerful, but more sensitive, explosive. Wet gun-cotton, for instance, is generally fired by means of a priming of dry gun-cotton, which in turn is exploded by a detonator. Picric acid when cast or compressed to a high density is almost as insensitive as wet gun-cotton: it is often exploded by

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[1] *See Deutsches Offizierblatt*, 1906, p. 513; Vennin et Chesneau, p. 382.

[2] *See* Pangher, *Mittheilungen über Gegenstände des Artillerie-und Geniewesens*, 1906 pp. 38–59; *S.S.*, 1906, 340.

[3] Prof. A. Keller, *Frankfurter Zeitung*, 1915.

means of a priming of picric powder, a mixture of ammonium picrate and saltpetre, or pellets of trotyl or tetryl may be used provided they are only compressed to a comparatively low density. Shell must, of course, be made so insensitive that they will not be exploded by the shock of discharge from the gun. Large fulminate detonators are therefore generally avoided, although they have been used by some of the Continental armament firms. When they are not used, it is necessary to have a priming that will burn to detonation when ignited by a small charge of gunpowder only. This priming is sometimes placed in a separate cavity formed in the middle or on the top of the charge in the shell: sometimes it is in a metal sheath or "gaine" attached to the bottom of the fuse. Use may also be made of a comparatively sensitive explosive such as tetryl, which is exploded by means of a small fulminate detonator.

It is not very easy to ensure the satisfactory detonation of shell filled with insensitive explosives, especially in the case of the smaller sizes of shell. The detonator and the exploder must be of sufficient strength. The intermediate explosive, or exploder, must be moderately sensitive and must be in close contact both with the detonator and the main charge of high explosive. If the whole of the charge is not consumed in the explosion the shell is said to "explode" instead of detonating. An "explosion" is revealed by the colour of the smoke that appears when the shell opens. If there be any unconsumed explosive the smoke will be more or less of the colour of the explosive, generally yellow. If the explosive be entirely consumed the smoke will be white or black according as it contains sufficient oxygen to oxidize the whole of the carbon present or not. The violence of the detonation can also be judged by firing a shell at rest in a closed chamber lined with steel plates and ascertaining the number and size of the fragments into which the shell is broken (*see* Fig. 122). This, however, is not considered so satisfactory a test as firing from the gun at a steel plate or other target, according to the nature of the shell. With practice the observers can form a good estimate of the violence of the explosion or detonation.

CHAPTER XXXIII

NAVAL AND MILITARY EXPLOSIVES

Demolitions : Gun-cotton : Direction of detonation : Military mines : Submarine mines : Torpedoes : Shell : Shrapnel shell : High-explosive shrapnel : Trench howitzer shell : Breaking wire entanglements : Chemical shell : Star shell : Tracers : Grenades : Rifle grenades : Flying machines : Incendiary bombs : Incendiary shell

Smokeless powder has already been dealt with in Part VII, but this is only one of the many varieties of explosive that are used in warfare. For many military purposes, such as mining and demolitions, the ordinary commercial blasting explosives can be used, but even in these cases dynamite and similar materials are objectionable because their sensitiveness makes them dangerous to the users under the conditions of active service. For other purposes, especially for filling shell, very insensitive explosives are absolutely essential.

Demolitions.

Gunpowder and similar mixtures are not very suitable for demolitions or mining, except in soft rock and earth. Their brisance is too low, and they require careful preparation of the hole for the charge and thorough tamping, which are often impossible on active service. When E. A. Brown had shown that wet gun-cotton could be detonated by means of a primer of dry gun-cotton, it was introduced into the British service, and was soon adopted by the other Powers. It possesses the advantage of being decidedly insensitive, and it can be detonated without confinement. Later picric acid was adopted by some of the Continental Powers, and still more recently trotyl (trinitro-toluene). Smokeless powder is also sometimes used for demolitions, when other explosives are not available, but it is difficult to detonate, especially the larger sizes, and has rather a low velocity of detonation. Ballistite is used in Italy to a considerable extent for this purpose. Captain Zschokke of the Swiss Army has given the following results of tests on some of the explosives that may be used for military demolitions :[1]

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[1] *Militarische Sprengtechnik,* 1911.

	POWER	SENSITIVENESS	BRISANCE
	Trauzl Test	Falling Weight Test	Crusher Test
	c.c.	cm.	Per cent.
Picric acid, compressed, sp. gr. 1·63	300	30	35·5
Picric acid, cast, sp. gr. 1·76	325	30	—
Trinitro-toluene, compressed, sp. gr. 1·50	300	80	31·8
Trinitro-toluene, cast, sp. gr. 1·61	260	80	—
Gun-cotton, 2 per cent. water, sp. gr. 1·12	323	25	21·0
Guhr dynamite (70 per cent. N/G)	316	20	23·4
Gelatine dynamite (75 per cent. N/G)	517	15	14·7
Blasting gelatine	632	15	9·1
Cheddite C (chlorate expl.)	378	20	21·0
Cheddite 60 N.	288	18–20	16·7
Cheddite 60	273	15–20	15·5
Cheddite 41	300	40	11·4
Westfalite (Am. nitr. expl.)	442	55–60	12·0
Smokeless powder (N/c 82, Tnt 18)	350	25	7·8
Petroklastite	157	100	—
Blasting powder	108	65	—

For most of the tests 2 g. detonators were used containing a little trinitro-toluene: only for trinitro toluene itself special ones were employed containing 2 g. of tetranitro-methylaniline. The falling weight tests were carried out with Lenz's apparatus with a 10 kg. weight falling on to a quantity of 0·15 to 0·2 g. (according to the density) pressed into a tablet 0·5 sq. cm. in area and 2·5 mm. high, wrapped in tin-foil. For the brisance test quantities of 10 g. were used. In the Trauzl tests on the last two explosives the charges were tamped with quick-setting cement. For further particulars concerning these various tests *see* Part IX.

The gelatine dynamite and blasting gelatine would, no doubt, have shown a higher brisance if they had been detonated by means of a powerful primer instead of a detonator only.

Gun-cotton. Gun-cotton for demolition purposes is compressed in powerful hydraulic presses. The moulded blocks or cylinders (*see* p. 187) are placed in the press and subjected to a pressure of 4 to 7 tons per square inch, whereby the height is reduced to about a third, and the moisture to about 15 per cent. The density of the compressed gun-cotton is from 1·05 to 1·20. The compressed gun-cotton is as hard as wood, and can be cut with ordinary wood-working tools, provided it be kept thoroughly wet. Use is made of this fact to shape slabs to be used for charging submarine mines and torpedo war-heads, also to drill holes in the primers to take the detonators. The primers are afterwards dried by means of hot air until they contain only about 1 per cent. of water, and finally they are waterproofed.

Picric acid. Many of the Powers use picric acid, which has a higher velocity of detonation and a higher density than compressed gun-cotton. Its power is slightly less weight for weight, but bulk for bulk it is greater. In Germany it is compressed to a density of 1·5 to 1·55, under the name of Sprengmunition 88, and made up in the forms shown in Fig. 120. To protect them against moisture and crumbling, the outer layers of the "Sprengkörper" and "Bohrpatrone" are impregnated to a depth of about 4 mm. with paraffin, and are wrapped in paraffined paper, and the hole for the detonator is closed with a disc of paper. The Sprengkörper weighs about 200 grammes, and the Bohrpatrone 75 grammes. The "Sprengpatrone" consists of five Sprengkörper in a tin box with holes on three sides for detonators and wires to bind them on. Picric acid of this density can be detonated directly by means of a 1 g. detonator, but it is better to use a more powerful one. In France, under the name of Mélinite, picric acid is made up into cylindrical cartridges weighing 100 grammes, and oblong boxes holding 60 grammes and 135 grammes and 20 kg. respectively.

Trinitro-toluene. Picric acid has two great disadvantages: it is liable to form highly sensitive picrates, if it comes in contact with basic substances, or metals other than tin, zinc, or aluminium, and if it is wet it loses its power of detonating. For these reasons there is a strong tendency to use trinitro-toluene instead of picric acid. The velocity of detonation, power and density of trinitro-toluene are all slightly lower, but not sufficiently so as to make much practical difference. In Germany, under the name of Sprengmunition 02, it is compressed to a density of 1·45 to 1·5 and made up into cartridges of the same dimensions as Sprengmunition 88. In Spain the same substance is used under the name of Trilit, and in France under that of Tolite: other fancy names are Trinol and Trotyl. Trinitro-toluene requires a more powerful detonator than picric acid: a 2 gramme detonator is not always sufficient, and it is better to use one containing a small quantity of a more powerful explosive in addition to fulminate.

There are other nitro-derivatives which have greater power and a higher velocity of detonation than trinitro-toluene, for example tetranitro-aniline, but their high cost of manufacture prevents their use on a large scale.

Direction of detonation. For demolitions carried out with unconfined charges it is important to remember that the action of the explosive is much more powerful in the direction in which the wave of detonation is travelling than in the opposite direction. The results obtained by Kast with the brisance-meter indicate that no useful purpose is served by increasing the length of the cartridges under these conditions to more than 75 mm. (3 inches).[1] It has been found by Neumann [2] that if a charge be hollowed out as shown in Fig. 121, the effect

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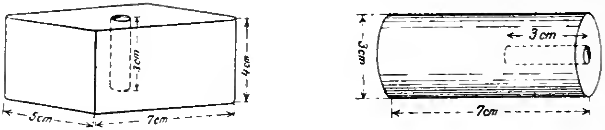
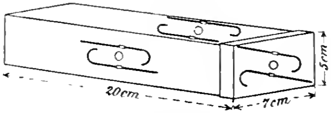
[1] *See* chap. xxxi.

[2] *Ang.*, 1911, p. 2238; *also S.S.*, 1914, p. 183.

is intensified considerably. The reason seems to be, that when the wave of detonation reaches the cone-shaped hollow, waves of compression start out perpendicularly to the conical surface, and these meet in the centre, producing a much greater effect than an ordinary detonation wave: just as there is an intensification of effect where two waves meet in a piece of detonating fuse.



Sprengkörper Bohrpatrone

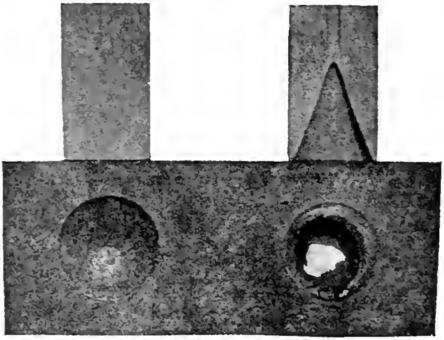


Sprengpatrone

FIG. 120. Dimensions of German Military Blasting Cartridges

Section of Complete Cylinder 310 g. Tnt

Section of Hollow Cylinder 247 g. Tnt



Wrought iron plate 25 mm. thick on which both charges were detonated in upright position

FIG. 121. Effect of Hollowing-Out a Charge

takes to a great extent.[1] The explosive for submarine mines must not only be very brisant but must also be very insensitive so that it cannot be exploded by a stray bullet or the fragment of a shell, else there would be great danger of the total destruction of any vessel engaged in laying mines during war time. Various devices are used to cause the mines to explode when struck by a passing ship, or diverted from a normal position, or they can be made to fire by an electric current actuated through a cable from an observation post on the shore.

Torpedoes. The name is borrowed from an electric fish and was applied at one time to submarine mines of all kinds. Now its use is restricted to mines provided with means of propulsion. The modern torpedo is driven by an air engine actuated by compressed air which is heated by means of a burner so as to increase the power. It is provided with a gyroscope to keep the direction constant. It is launched from a tube by a charge of smokeless powder, travels with a speed of 30 to 45 knots, and has a range of 10,000 to 11,000 yards (6 miles). In the head there is a charge of about 200 lbs. of high explosive, usually trotyl. On reaching its objective a pistol mechanism in the nose of the torpedo fires and causes the charge to detonate. The firm of Whitehead in Fiume has patented an arrangement by which the charge in the war-head is detonated from the rear, so that the wave of detonation travels towards the wall of the ship attacked. With this arrangement they have obtained decidedly better results than when the detonation wave is started from the nose.

Shell. As a filling for shell, black powder was used almost exclusively until a comparatively late date, as its insensitiveness to mechanical influences enables it to withstand the shock of discharge with safety, and even if it explodes in the gun it does not do any serious damage. It is still used for Shrapnel, as it possesses ample power to drive the bullet out of the shell casing, and the smoke it produces is an advantage, in that it enables the artillerymen to see where the shell burst. It is also used for star shell and other special varieties of shell.

Soon after the discovery of gun-cotton attempts were made to use it for filling shells, especially in Austria, but it has never met with much favour for this purpose. Wet gun-cotton is very difficult to detonate, and if there be a priming of dry gun-cotton there is danger of premature explosions. Nitroglycerine explosives have not been much more successful. Austria has tried blasting gelatine "phlegmatized" with camphor, but even so it must be dangerously sensitive; moreover, even without the addition of camphor it is not easy to obtain the maximum velocity of detonation, and the stability falls off rapidly on keeping. Italy is said to have used Ballistite, to which the same objections may be raised, except that it is not mechanically sensitive.

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[1] *See also* K. Pramer, *Mittheilungen aus dem gebiete des Seewesens*, 1914; *S.S.*, 1915, p. 116.

Military mines.

For military mines the explosives used must depend largely on the nature of the ground or rock. In soft rock or earth gunpowder could be used, but a great weight is required to produce the same effect as a smaller quantity of many other explosives. It also has the disadvantage that on explosion it gives a considerable quantity of carbon monoxide. Ammonal has been much used in Flanders: [1] if it contain a sufficient proportion of ammonium nitrate it gives rise to no noxious fumes.

Submarine mines.

For submarine mines and torpedo war-heads the requirements are much the same as for military blasting. As long ago as the Crimean War (1854–1856), Emmanuel Nobel, the father of Alfred Nobel, is said to have used mines charged with gun-cotton to protect the mouth of the Neva. Mines were also used to some extent in the American War of Secession (1861–1865). From 1869 onwards the problems connected with the destruction of vessels by submarine explosives were investigated by General Abbott of the U.S. Army. He found [2] that brisant explosives, such as dynamite, blasting gelatine and gun-cotton produced the greatest effect; that it was not necessary to enclose the charge in a very strong shell, and that immersion at a depth of 3 to 5 feet was sufficient to ensure a good effect. Formulae for calculating the pressure exerted according to the distance, the weight of charge, and direction have been given by Abbott and also by Colonel Bucknill.[3] In these old experiments, however, the pressure was measured with a crusher. Blochmann has used a dynamometer which gives a curve showing the variation of the pressure with the time (*see* Fig. 104, page 502).

The pressure due to the explosion is very great in the immediate neighbourhood of the charge, but it falls off as the distance increases, at first very rapidly, but more slowly at considerable distances. The following figures were given by Baron Roenne in a paper before the Royal Service Institution in November, 1911, for the pressures in kg. per sq. cm. due to 100 kg. of gun-cotton (density 1·11):

Distance cm.	Percussive Pressure	Pressure due to gas
0	1801	8900
25	527	2480
50	232	1147
100	85	426

It is supposed that the percussive force first breaks through the wall of the ship and then the gas pressure causes a great inrush of water. Even at quite moderate depths the path through the ship offers less resistance than the water above the submarine mine, and therefore this is the path that the explosion

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[1] C. G. Martin, *Jour. Roy. Art.*, 1916, p. 111.

[2] *Paper* 23, U.S. Corps of Engineers, 1884.

[3] *Engineering*, 1887 and 1888.

The first satisfactory solution of the problem was the adoption of picric acid by France. This was quickly followed by similar measures taken by practically all the other Powers, each of whom, however, gave the substance a different name :

France	Mélinite
England	Lyddite
Germany	Granatfüllung 88
Italy	Pertite
Japan	Shimosite
Sweden	Coronite
Spain	Picrinite

Under the name of crésylite 60/40, of crésylite No. 2, the French also use a mixture of 60 parts nitrated cresol with 40 parts picric acid. This mixture, which is made by melting the substances together under water, has the advantage of melting at about 85°, and of being very plastic at a temperature of 65° to 70°. The molten explosive is filtered, poured on a table, granulated when cold, and dried at 45°.[1]

The Austrians have used the ammonium salt of trinitro-cresol under the name of Ecrasite, but are said to have given it up again in consequence of some accidents.[2] The United States of America have adopted a preparation of picric acid under the name of Dunnite.

Picric acid is now being replaced everywhere with trinitro-toluene for the same reasons that have caused the latter to be used for demolitions, and also because its melting point is much lower.[3] When picric acid is detonated, a part of the carbon separates as such, producing black smoke, and trinitro-toluene gives rise to a larger proportion. This involves a considerable diminution in the volume of gas formed, and also in the heat evolved, and consequently the power is not so great as if all the carbon and hydrogen were oxidized. The trotyl is therefore sometimes mixed with an oxidizing agent, a list of which is given on p. 4. In Belgium Macarite has been used, which is a mixture of trotyl and lead nitrate in the proportion 30 : 70. Lead nitrate possesses the advantage of a very high density. The fumes given off on explosion are somewhat poisonous, but most of the explosives used for shell evolve carbon monoxide, which also is poisonous. In Austria ammonal is used, a mixture of trotyl, ammonium nitrate, charcoal and aluminium powder. A sample analysed by Poppenberg and Stephan [4] had the composition :

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[1] Vennin et Chesneau, p. 280.

[2] Chalon, p. 133

[3] In the British service trinitro-toluene is called Trotyl or TNT ; in the German, Füllpulver 02 or Fp 02.

[4] *S.S.*, 1910, p. 311.

Trotyl	18·0
Ammonium nitrate	58·6
Charcoal	2·4
Aluminium	21·0

The French also use for their high explosive shell Schneiderite, which according to Bethel has the composition:

Ammonium nitrate	88
Dinitro-naphthalene	11
Resin	1

It is therefore somewhat similar to Grisounite No. 1 c. (*see* p. 389). There are many other ammonium nitrate mixtures that might be used.[1]

The ammonium nitrate makes these mixtures very hygroscopic. This must give trouble in peace time, when the shell have to be kept many years before they are fired, but in war time the charge in a shell would have little time to absorb moisture before it would be expended. Ammonal is said to be so insensitive to blows that it can be fired in shell through the armour plating of a warship without exploding. Other additions have been made to trotyl to diminish its sensitiveness: Plastrotyl contains a small proportion of resin, and Triplastite consists of a mixture of trotyl and lead nitrate made plastic by means of liquid dinitro-toluene gelatinized with collodion cotton.

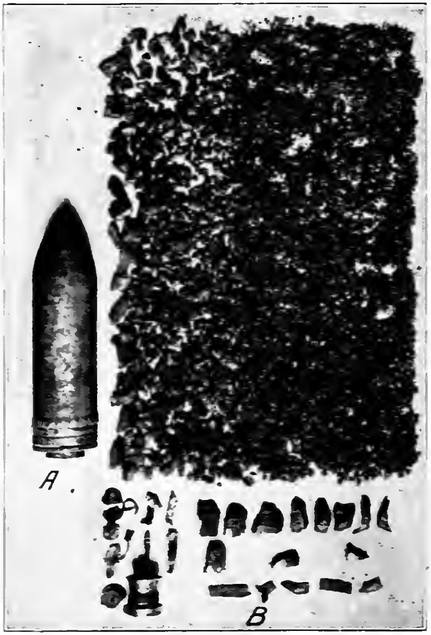

FIG. 122. 3-inch High Explosive Shell

A. Recovered from sand butt after firing through a steel plate.

B. Fragments resulting from high explosive bursting charge.

(From paper by Maj. E. P. O'Hern in *Smithsonian Report*, 1914. p. 265.

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[1] *Jour. Roy. Art.*, vol. xl., 1913, p. 301. *See also* N. W. Berger. *S.S.*, 1906, p. 150.

In consequence of the scarcity of nitrates in Germany preparations are apparently being made to use cheddite in shell, if indeed it is not being used already.

Armour-piercing shell For the attack of warships shell are required that will pass through the armour and explode when they are on the other side. By providing the shell with a cap of soft iron to protect its nose, and by suitable construction, the mechanical difficulties of obtaining a projectile which can perform this feat without breaking up have been overcome to a great extent. It is necessary also that the explosive shall be so insensitive that it will not be exploded by the tremendous shock caused by the impact of the shell on the armour at a velocity of perhaps two thousand feet per second. Black powder fulfils this condition, and until recently armour-piercing shell were generally filled with it. Ammonal and other ammonium nitrate explosives are said to be sufficiently insensitive. Fig. 123 shows an American armour-piercing shell with base fuse, cap, and a false point to make the shell more pointed and consequently reduce the resistance of the air. Fig. 124 shows a similar shell after proof.

In the construction of shell and their fuses great care must be exercised to prevent premature explosions. In the case of shell charged with gunpowder a premature explosion is dangerous to friendly troops stationed in front of the gun, but in most cases does no damage to the gun. The detonation of a high explosive shell in the bore, on the other hand, invari-

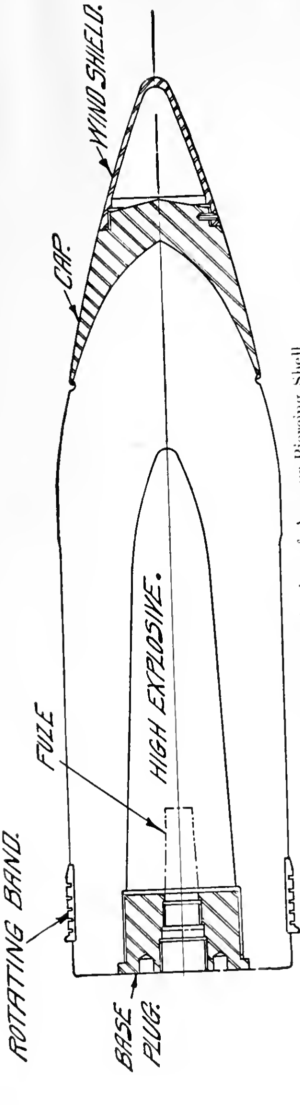

Fig. 123. Section of Armour-Piercing Shell

(From paper by Maj. E. P. O'Hern in *Smithsonian Report*, 1914, p. 260.)

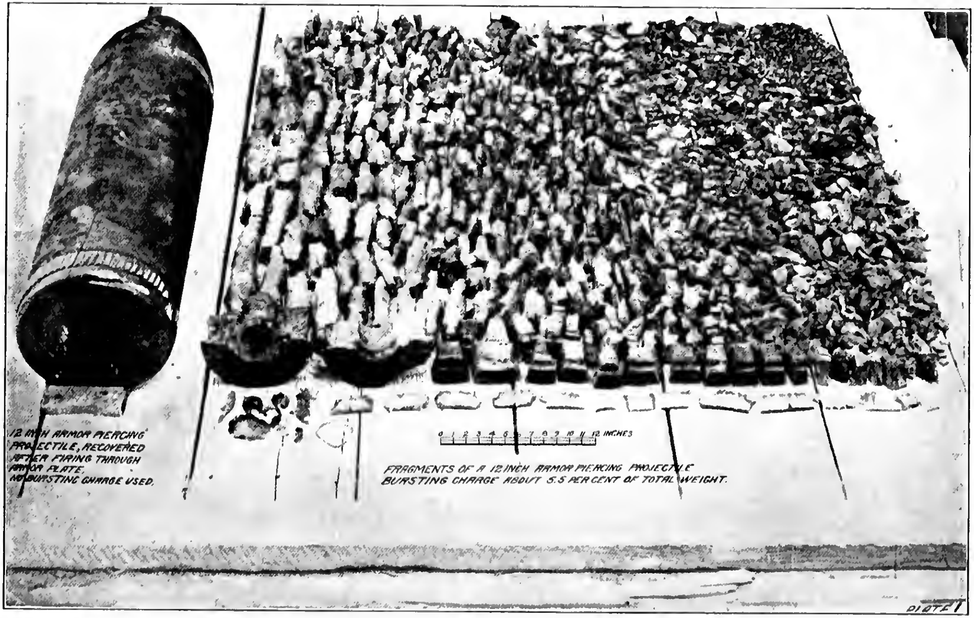

FIG. 124. Armour-Piercing Shell after Proof
(From paper by Maj. E. P. O'Hern in *Smithsonian Report*, 1914, p. 250.)

ably puts the gun out of action. Hence the necessity for making the walls and base of the shell of metal that is above suspicion and of sufficient strength, and of providing the fuses with safety arrangements. Howitzer shell are fired with small charges of powder at comparatively low velocities: therefore the shock of discharge is less and the walls of the shell can be made thinner, and the charge of high explosive greater in comparison.

The weight of the bursting charge forms 5 to 25 per cent. of the total weight of the shell. The German howitzers are provided with two sorts of high explosive shell: common high explosive shell and mine shell.[1] The common shell is used against an enemy under cover, who are struck by the fragments of the walls, which mostly fly off at right angles to the axis of the shell when the charge detonates. The walls of these shell are thick. Those of the mine shell are made as thin as possible without incurring the risk of the shell breaking up in the bore of the gun. The charge of high explosive in the mine shell is as great as possible, and the shell are used for the destruction of material obstacles such as fortifications. The shell are provided with impact fuses. The Krupp 10·5 centimetre (4 inch) howitzer, for instance, fires shell weighing 14 kilogrammes; of these the common shell has a charge of 1·4 kg. and the mine shell of 2·8 kg. The impact fuses of mine shell are provided with a delay arrangement so that they do not detonate until a few hundredths of a second after striking, and have time to bury themselves.

Shrapnel shell.

Shrapnel shell consists of a comparatively thin-walled steel casing, the greater part of which is filled with bullets embedded in resin. Formerly sulphur was sometimes used instead of resin. In the base there is a chamber containing a small charge of gunpowder, and this is connected with the time and percussion fuse in the nose by means of a channel filled with gunpowder pellets. The charge chamber is separated from the bullets by a stout steel diaphragm. According to the setting of the time fuse the charge explodes at a known time from the discharge of the gun. The pressure generated by the powder bursts off the nose of the shell, and the bullets are driven out of the shell casing in a cone of 15° to 30°. Consequently, if the burst has been well timed and the direction of the gun has been correct, the bullets will sweep over a considerable area. These shell are very effective against troops in the open, but under modern conditions infantry entrenches whenever possible, and artillery is provided with shields and generally fires from concealed positions. Consequently shrapnel has lost much of the importance that was assigned to it, and has been replaced by high explosive shell to a great extent.

High-explosive shrapnel

In order to avoid the complications caused by providing batteries with two sorts of shell, shrapnel and high explosive, which moreover do not range equally, universal shell have been introduced, which can be used for both purposes. In the Ehrhardt universal shell (Fig. 125) the high explosive charge is

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[1] Prof. A. Keller, *Frankfurter Zeitung*, 1915.

in the head. When exploded by the shrapnel time fuse the head flies on in front of the bullets, and when it strikes an object it is detonated by the impact

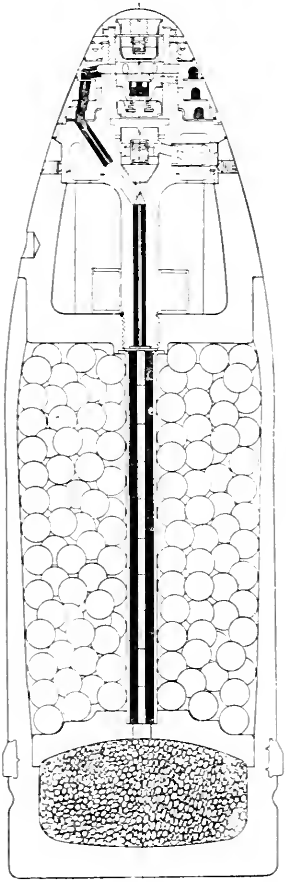
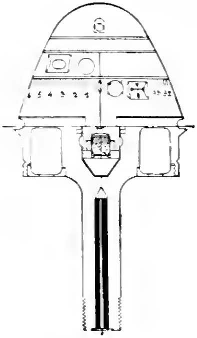


Fig. 125. Ehrhardt Universal Shell 4·2 in. Howitzer

(Einheits-geschoss, 10·5 cm. Haubitzer)



Fuse.

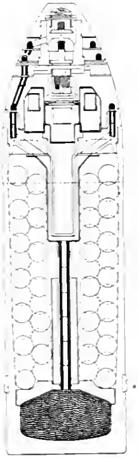


Fig. 126. Krupp Universal Shell with Quadruple Action Fuse

Breaking wire entanglements.

fairly thick walls as the wire is cut principally by flying fragments and not to any great extent by the direct blast of the explosion. Ordinary shrapnel shell and high explosive shell are used for the same purpose. Proposals have also been made to clear a passage through a wire entanglement by pushing through it a tube charged with high explosive and then firing it.[1] The tubes are made for convenience in sections which are joined together on the spot.

Chemical shell.

The use of poisonous gases and vapours by the Germans has rendered it necessary for the opposing Powers to adopt similar measures. Chemicals of various sorts are therefore fired in shell as well as being released from pipes and cylinders. Such shell have a small opening charge of a mild explosive such as gunpowder, fired by means of a fuse in much the same way as shrapnel.

Star shell.

For illuminating the country at night, and also for signalling purposes shell are made similar to shrapnel, but with stars of firework composition instead of bullets. There are from two to twelve stars, carefully packed in to prevent damage by the shock of discharge. They are generally filled with a light-giving composition similar to the flashlight powders used in photography, namely, mixtures of magnesium or aluminium powders, or both, with potassium nitrate or perchlorate or barium nitrate, with or without some binding material. In some of the more recent star shell each star is fitted with a parachute which opens when the shell bursts and prevents the star falling too rapidly.[2] Star shell are provided with time fuses; when the fuse has burnt the proper time it ignites the priming of the stars and also the bursting charge in the base of the shell.

Tracers.

It is often desirable to be able to observe the course of a shell through the air. This is especially the case when attacking airships. For this purpose J. B. Semple devised "tracers," which are fitted into or on to the base of the shell. For use by day the tracer is filled with a dark coloured liquid, which is ejected during flight as a fine spray. The night tracers are filled with a firework mixture, which is ignited as the shell leaves the gun, and renders the course of the projectile visible like that of a rocket.[3]

Grenades.

The hand-grenade, which was introduced in the seventeenth century, and was very largely used during the wars of the eighteenth, lost its importance in the time of the Napoleonic wars, but its use did not cease entirely, for it was employed in 1808–1809 at Saragossa, in 1832 at Antwerp, in 1854–1856 at Sebastopol, and in 1884–1886 by the English in the Sudan. During the Russo Japanese War (1904–1905) the hand-grenade regained much of its old importance, and in the present trench warfare they are used in immense numbers.

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[1] *See S.S.*, 1915, p. 31.

[2] *See* F. Krupp A.-G. Germ. Pats. 246,411 of June 21, 1910; 264,476 of February 6, 1912; 268,324 of October 6, 1912; 272,115 of June 2, 1912.

[3] *See* Germ. Pat. 261,580 of March 15, 1911.

portion of the fuse. If the shell reaches its billet before the time fuse has functioned, the impact fuse acts and detonates the trotyl, which scatters all the components of the shell. In the Balkan War it was found that the heads of the universal shell were liable to burst in the air when the shrapnel charge of gunpowder was set off by the time fuse. The makers therefore added a small bursting charge between the bullets and the head, so as to blow the head off before the main burster had time to act.

In the Krupp high explosive shrapnel (Fig. 126) the bullets are embedded in trotyl instead of resin or sulphur. Space is thus saved. When the charge in the chamber in the base explodes it drives out the bullets in a cone together with the trotyl which is partly burnt. But by setting the fuse in a different way the trotyl can be made to detonate. The charge in the base is said to consist of an explosive which will also detonate under the influence of the trotyl, although when merely ignited it only explodes. The fuses of these shell are necessarily somewhat complicated, but advantage is generally taken of the fact that the shrapnel effect is mostly required with a time fuse, and the high explosive on impact. Such shell are very expensive compared with common high explosive shell or even with ordinary shrapnel, and as the number of shell required in warfare is now so enormous, their use is restricted. However, the German light field howitzer of 10·5 cm. calibre, in consequence of the many purposes for which the weapon is used, is provided with a universal shell, which according to the adjustment of the fuse can be used either as shrapnel, as common shell without delay for attacking troops under light cover, and with delay as mine shell for the destruction of strong works. The German 7·7 cm. field gun also fires high explosive shrapnel sometimes.

Trench howitzer shell.

Trench warfare has led to the use of numerous appliances which had before received little attention. Amongst these is to be numbered the trench howitzer, which from a trench or other concealed position throws a shell of considerable calibre with a comparatively low velocity. In some types of trench mortars the shell are of considerably greater diameter than the gun, and have a stick which goes down the bore. Such shell often have spiral wings fixed to their bases to keep the shell nose on during flight and give it a rotary motion. These are sometimes called aerial torpedoes. Other shell have, fixed to their bases, tubes which fit over an adjustable bar on the gun. The propulsive charge is placed in the tube between its end and the end of the bar. When this is fired it causes the tube and the shell fixed to it to travel in the desired direction. As the shock of discharge of a trench mortar is comparatively slight the shell do not require to be constructed so strongly as those for ordinary guns and mortars. Somewhat more sensitive explosives can be used; the Germans use sometimes explosives of the Astralite type containing a little nitro-glycerine.

Trench mortars are often used to assist in breaking the enemy's wire entanglements. For this purpose it would appear advisable to use shell with

The hand-grenade of the eighteenth century was a hollow iron ball, about 2½ inches in diameter, containing a charge of gunpowder. It had a fuse of slow match which ignited the powder a few seconds after it had been lit and thrown. In 1882 the French adopted a spherical-grenade 8·12 cm. in diameter (3·2 inches) with walls 9 mm. (0·35 inch) thick, and containing a charge of 110 grammes (4 oz.) of black powder. It weighed 1·2 kg. (2·64 lbs.). The ignition mechanism consisted of a friction pellet, through which passed a wire with a loop at the other end. The thrower passed through this a hook which was attached by means of a cord to a band round his arm. The wooden fuse contained some slow burning composition which prevented the grenade exploding until several seconds after the friction pellet was ignited by the withdrawal of the wire in the act of throwing the bomb. Towards the end of the nineteenth century the Russians introduced a similar hand-grenade.[1] Grenades of this pattern are in use now, except that the charge consists of high explosive instead of gunpowder. As a hand-grenade does not have to withstand the shock of discharge from a gun, many patterns can be used which would be impossible in the case of shell. Both in the Russo Japanese war and in the present conflict various patterns of improvised bombs have been used. These are often made of jam tins, artillery cartridge cases or empty shrapnel shell filled with explosive, with the addition of nails or odd bits of iron to act as missiles. Another type is that of the "hair-brush." This consists of a piece of wood shaped like the back of a hair-brush, on which is laid a slab of guncotton or other high explosive, and on that again some long nails, the whole being bound together by means of wire. Such bombs as these containing comparatively large charges of explosive produce considerable moral effect, but are not so deadly as grenades with strong iron or steel walls enclosing a smaller charge.

The grenades that are not improvised, but manufactured in a regular way, conform generally to two different types: Firstly the "cricket ball" or "egg" type resembling the old grenade or that shown in Fig. 128. The other is a cylindrical or oval bomb attached to a handle to facilitate throwing it. This type is often known as the "policeman's truncheon." The Hale hand-grenade is of this class. In the early patterns the explosive was contained in a brass tube, round one end of which was a ring of iron or lead with grooves in it to make it split into segments. But in later patterns the container itself is of stout cast steel, and there is no ring. Fig. 127 shows a grenade of this type which was devised by Captain Lischin in 1904, and used by the Russians in the battle of Mukden. It was charged with dry gun-cotton, C, and a 1 gramme detonator. The cap, D, could be removed to permit the insertion of the detonator, and it could be turned so as to make the grenade either live or safe. As a further precaution the cap, K, was kept on until the

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[1] Major Andersch, S.S., 1913, p. 24.

grenade was used. In more recent bombs of this type the second cap is done away with, and for it is substituted a safety pin, which is withdrawn just before throwing. Also trotyl or other high explosive is used instead of guncotton, and there is an exploder between the detonator and the charge. On impact the pin, O, is driven into the detonator and fires it. The wooden handle, B, is about 18 inches long, and often has attached to it a tail of some fabric to cause the grenade to travel nose first.

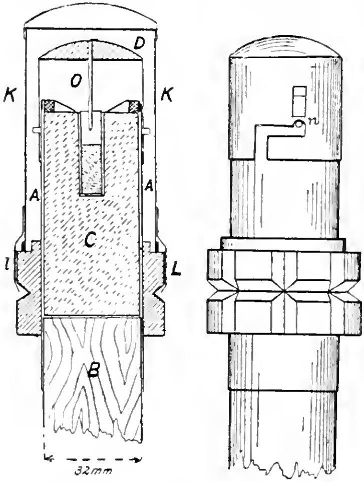

Fig. 127. Lischin's Hand-Grenade. Truncheon Type
(From *S.S.*, 1911, p. 433)

The fuses of hand-grenades may be made to act either by time or percussion. A time fuse is usually arranged to fire the grenade in about five seconds, which gives sufficient time for throwing the grenade but not enough for the enemy to throw it back. The disadvantage of the time fuse is that if for any reason the bomb be not thrown almost at once it may be fatal to the thrower and his companions. There is a report of a soldier in the Dardanelles who caught the grenade against the edge of his own trench so that it fell back at his feet. As there was nothing which he could place over it he promptly sat on it and so sacrificed his own life for that of his fellows.

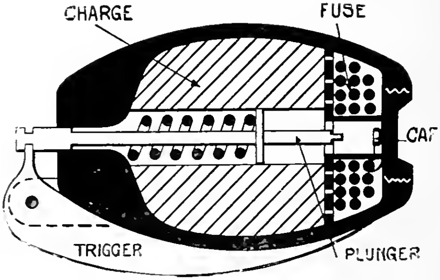

Fig. 128. Mills' Hand-Grenade. Egg Type
(From *Manual of Explosives*, by A. R. J. Ramsey and H. C. Weston)

The methods of lighting the time fuses are various. One of them has been described above. Another is to provide the end of the fuse with a match head, which is rubbed on a prepared surface just before the bomb is thrown. Or the fuse may be started by removing a safety disc and striking the head of the grenade against an obstacle. Others again are started automatically by the act of throwing the bomb.

In the Mills' hand-grenade (Fig. 128) the time fuse is started by releasing the lever or trigger in the act of throwing. There is also a safety pin which is removed just before use. When the trigger is released the spring causes the striker to impinge on the cap, which ignites a length of about 2 inches of fuse, and this after about five seconds fires the detonator, which detonates the charge.

The impact fuse also suffers under disadvantages. It is not easy to make sure that the grenade will always fall on its nose, although they are often provided with a tail consisting of strips of cloth or similar material, and it is difficult to make a fuse that will act if the missile falls on its side or base. Moreover, there is always danger that the thrower may hit the grenade against the walls of the trench and so kill himself and his fellow soldiers. All grenades must be provided with some safety device which is removed by the thrower just before he throws it. But many also have a further ingenious mechanism of some kind which prevents the grenade becoming active until it has travelled some little distance. One of the difficulties lies in the fact that grenades are often required to act at very short range, as when they are just dropped over a traverse in a line of trenches. The modern hand-grenade has not yet been in use long enough for finality to be reached in the designs.

For filling hand-grenades almost any high explosive could be used, but the more insensitive it is, the safer it is under the very severe conditions of active service. The explosives actually utilized are practically the same as those used for artillery shell. Cheddite and ammonal are also used.

Rifle grenades.

Grenades are also made to throw with a sling or catapult, and there are rifle grenades, such as that of Hale, which can be fired from a rifle to a distance of a few hundred yards. The rifle grenade has a rod which goes down the barrel of the rifle, and it is fired with a special cartridge having no bullet. A safety pin is removed before firing, but the grenade does not become live until it has travelled some distance and some vanes attached to it have by rotating released the striker, which on impact hits the detonator.

Flying machines.

In the case of bombs to throw from flying machines there is not the same limitation as to weight. The principal difficulty here is to attain a sufficient precision without approaching the enemy so close as to place the aviators in great danger. Some ingenious appliances have been designed for sighting the dropping mechanism, but the accuracy is much lower than that of a gun. As an aeroplane can only carry a few bombs it is necessary to employ a considerable number of aeroplanes to ensure hitting a specified object, unless it be of great size. Aeroplane bombs are fitted with a safety arrangement which only allows the detonating mechanism to come into action after the bomb has fallen a considerable distance. This may take the form of a vane rotated by the air until it releases a striker, which on impact strikes the detonator.

For the attack of flying machines special guns are made of extra high muzzle velocity and high angle fire. For the destruction of Zeppelins and other dirigibles endeavours are made to set light to the hydrogen of the balloons, but this is not so easy as it seems, because the projectile passes the envelope so rapidly that it has little time to ignite the gas at the spots where it enters and leaves.

Incendiary bombs.

Flying machines are frequently provided with incendiary bombs for the destruction of property. These may be charged with inflammable substances such as petrol, tow steeped in tar or celluloid, together with some match composition which ignites on impact or at a fixed time after the bomb has been dropped. Another substance used for incendiary bombs is thermit, a mixture of iron oxide and aluminium or other similar materials. On strong ignition a chemical reaction sets in with large evolution of heat, producing a white-hot molten mass of metal and slag. A small charge of explosive is also added sometimes to scatter the incendiary materials.

Incendiary shell.

Incendiary shell are also made containing thermit or other incendiary matter, and a small charge of a mild explosive, such as gunpowder; to open the shell.

CHAPTER XXXIV

COMMERCIAL HIGH EXPLOSIVES

Hard rock : Soft rock : Miscellaneous : Blasting under water : Agriculture : Hailstorms : Dimensions of cartridges : Raw materials available : Oxyliquit : Grist : English statistics : American statistics : Products from explosives : Carbon monoxide : Nitrogen oxides : Acrolein, prussic acid, nitro-glycerine : Hydrochloric acid : Hydrogen sulphide : Stemming

Hard rock.

The principal factors which govern the choice of a blasting explosive for a specific purpose are the power, velocity of detonation, density and price. The sensitiveness, stability and the nature of the products formed must also be taken into account in some cases. These different factors assume varying degrees of importance according to the circumstances. For blasting very hard rock, such as gold quartz, a very brisant explosive is required; and on account of the expense of drilling, it must give a maximum of power in a minimum of volume. Blasting gelatine possesses all these qualities in a high degree, provided that it be fired with a very powerful detonator or primer, but if fired with a detonator of only moderate power, its velocity of detonation is only about 1500 metres per second instead of about 7000. To a less extent this also applies to gelignite and other similar gelatinized nitro-glycerine explosives, and accounts for the preference given in America and South Africa to non-gelatinized mixtures, which are not looked upon with favour by the authorities in England on account of the danger of exudation. It would seem that these very hard rocks would be blasted best with a charge of blasting gelatine provided with a primer of non-gelatinized nitro-glycerine explosive, such as American straight dynamite or Ligdyn.

Tonite.

A high explosive that was much used formerly is Tonite, which consists of gun-cotton mixed with a nitrate, and compressed into blocks or cylinders. It sometimes contains some trinitro-toluene. A Belgian Tonite with which Watteyne carried out some experiments[1] had the composition:

Gun-cotton	53·0
Barium nitrate	37·6
Sodium nitrate	9·4

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[1] *S.S.*, 1913, p. 427.

The Tonite made by the Cotton Powder Company consists of equal parts of gun-cotton and barium nitrate.

Tonite has now been replaced to a large extent by other explosives.

Soft rock. With softer rocks the expense of drilling is less; the bore-hole can consequently be made larger, and the density and power of the explosive are not so important. In Great Britain gelignite is the high explosive most used for this class of work, but ammonium nitrate and chlorate explosives are also much employed. If it be desired not to break up the material too much, a very high velocity of detonation is a disadvantage, and care should be taken not to overcharge the holes. For soft material such as coal, which it is not desired to break up too much, a mild explosive is best. Hence the popularity of Bobbinite. When the condition of the material is unimportant, as in the case of carnallite in the German potash mines, the principal consideration is to obtain the maximum power for the money spent. Sprengsalpeter is therefore much used for this purpose. Its slow rate of explosion is said, moreover, to be of advantage.

In America it has been found that 60 per cent. gelatine dynamite gives as good results as higher grades of blasting gelatine unless the rock be extremely hard and tough.[1] For tough granite and hard boulders 60 per cent. straight dynamite is used, for rock of moderate toughness 50 per cent., and for hard earth or sandstone 20 to 30 per cent. Judson powder is used for soft, crumbly or seamy rock, and black powder for soft earth, or in quarries where blocks of considerable size are required. Ammonia dynamites are employed where a heaving effect is desired.

Miscellaneous. For breaking up iron or steel castings a very brisant explosive is required, as also in all cases where it is impracticable to tamp the charge well. For torpedoing oil-wells also a violent explosive such as dynamite is used. For breaking up ice, a mild explosive such as gunpowder should be used if it be desired to obtain the ice in large lumps.[2] If, however, it be required to break a passage through an icefield, by placing charges on or in the ice, a brisant explosive is required. When the charge can be placed under the ice a mild explosive such as gunpowder or blasting saltpetre is better.[3]

Blasting under water. For blasting rock under water a brisant explosive is required, and the cartridges should be thoroughly waterproofed unless the explosive contains a considerable percentage of gelatinized nitro-glycerine. In cold weather there is great danger of the nitro-glycerine freezing after the cartridges have been placed in the bore-hole under water. Extra strong detonators should therefore be used. Under water an explosive produces considerably less effect

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[1] C. E. Munroe, *U.S. Bureau of Mines Bulletin*, No. 80.

[2] *S.S.*, 1906, p. 430.

[3] D. W. Stavenhagen, *S.S.*, 1906, p. 43.

upon the rock than it would on land, for the pressure of the surrounding water lends support to the material that is being blasted.[1]

Agriculture.

Of late years there has been a great increase in the use of explosives for agricultural purposes: for breaking up hard sub soil, removing tree-trunks, digging ditches, etc. If the charge can be tamped well, non-detonating explosives, such as blasting powder, would probably be the most economical on account of their low price, and the fact that the cost of the detonator is saved. In many cases, however, the ground is so unresistant that it is better to use a detonating explosive.

Hailstorms.

Some years ago there was much talk of preventing hailstorms by bombarding the sky with high explosives, the idea being that the shock would cause the moisture to be precipitated as rain instead of hail. Much money was spent on endeavours of this sort in the vine districts of Styria, Italy, and France, and there were loud claims of great successes, but later on the enthusiasm waned and died: in fact many of the previous advocates of the shooting came to the conclusion that it actually made the hailstorms worse. Be that as it may, an experimental inquiry carried out on a very large scale on behalf of the Italian Government led to the conclusion that the shooting did absolutely no good.[2] The same applies to the production of rain. Experience during the present war shows that even the most intense bombardment has no perceptible effect on the weather.

Dimensions of cartridges.

In consequence of the large number of different weights and sizes of cartridge demanded by different consumers Capt. Lloyd at the 7th Inter. Cong. Appl. Chem. (1909) proposed that they should only be made of the following dimensions:

	Weight	
	Grammes	Ounces
No. 2	50	2
,, 3	75	3
,, 4	100	4
,, 6	150	6
,, 8	200	8
,, 16	400	16

Size	Diameter mm.	in. (approx.)	
2	22	⅞	Common size for gelatinous explosives.
3	33	1¼	To take the place of 1⅛ in. and 1⅜ in. the commonest sizes for granular and bulky explosives.
4	44	1¾	For soft rocks and coal.
5	55	$2\frac{3}{16}$	For heavy charges.

Using the weight as numerator and the size as denominator the most

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[1] *See* Hall and Howell, *U.S. Bureau of Mines Bulletin*, No. 48

[2] *See* Blaserna, *P. et S.*, vol. xiv., p. 76.

common cartridges of gelatinous explosives would be: 2/2, 3/3, 4/3, 6/4, 8/4; and more rarely: 3/2, 2/3, 4/4, 8/5, 16/5. For granular and bulky explosives the commoner dimensions would be: 2/3, 3/3, 4/3, 4/4, 6/4; and occasionally: 6/3, 8/4, 6/5, 8/5.

To a large extent this proposal has been put into execution. Since March 31, 1913, in certain mines in the United Kingdom cartridges are only allowed to be used if they are of the diameter $\frac{7}{8}$, $1\frac{1}{4}$, $1\frac{7}{16}$, $1\frac{3}{4}$ or 2 inches. Further, no drill shall be used for boring a shot-hole unless it allows a clearance of at least $\frac{1}{4}$ inch over the diameter of the cartridge to be used.[1]

Raw materials available.

The price of the raw materials is a very important factor in the decision as to what constituents shall be used in the manufacture of explosives. Only inexpensive substances can compete with those already in use. There must also be sufficient quantities of these materials available. The present war has brought about some changes due to the failure of supplies of certain of the raw materials previously used on a large scale for the manufacture of explosives. In England sodium nitrate has in some cases been substituted for potassium nitrate. In Germany nitrates have become scarce in consequence of the stoppage of the delivery of sodium nitrate from South America. To a great extent this scarcity has been met there by the erection of large plants for the manufacture of nitrates from the air, but the produce of these plants is required for making military explosives, and there has consequently been a great development in the production and use of explosives not containing nitrates or nitro-compounds, or only containing them in small proportions. On March 20, 1915, all the Chile saltpetre in Germany was commandeered at a price of 240 marks per kg., and steps were taken to encourage the production of chlorate and perchlorate explosives.

Oxyliquit.

For the same reason liquid oxygen explosives have received renewed attention in Germany. In 1895 Professor F. C. Linde discovered that a mixture of liquid oxygen and various organic or carbonaceous materials could be detonated, and he gave the explosive thus made the name of Oxyliquit. It possesses several advantages: it is cheap, for liquid oxygen can be produced at a cost of a few pence per kg.: it can be fired with safety fuse without a detonator, and in the case of a missfire the charge becomes quite safe in half an hour in consequence of the evaporation of the oxygen. It was tried on a large scale in 1899 in the construction of the Simplon tunnel. The cartridge consists of kieselguhr mixed with petroleum, or of absorbent cork charcoal, in a suitable envelope. Liquefied air rich in oxygen is obtained from a liquefying plant near at hand, and the cartridge is dipped into this just before use. The charging, tamping and firing of the charge must be carried out rapidly before too much of the oxygen has evaporated. This is the principal objection to the method, and until recently has prevented its adoption, but

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[1] *Explosives in Coal-Mines Order,* May 21, 1912; *A.R.*, 1912, p. 32.

the necessities of war have led to its revival, and possibly the extended experience thus gained may lead to its retention in times of peace. L. Sieder recommends the use of a cartridge case so constructed that the oxygen gas given off has to travel backwards and forwards the whole length of the cartridge several times, thus hindering the absorption of heat by the very cold explosive. A cartridge of this sort, 38 mm. ($1\frac{1}{2}$ inch) in diameter, retains sufficient oxygen for 8 or 10 minutes to permit of full detonation. It is charged with a mixture of 40 per cent. petroleum and 60 per cent. guhr; a cartridge 200 mm. long weighs 91 grammes before steeping in liquid oxygen, and 295 grammes immediately afterwards.

In the process of Kowatsch and Baldus the liquid oxygen is not introduced into the cartridge until the charging of the bore-hole is otherwise complete. The cartridge is provided with two small tubes, one for the introduction of the liquid oxygen and the other for the escape of gas. The can in which the liquid oxygen is kept is closed except for a spout. This is connected with one of the tubes of the cartridge, and then the can is tipped up, whereby the liquid is forced out by the vapour pressure. The filling is continued until liquid oxygen comes out of the other tube. It is objected to this process that in the case of very deep bore-holes the charging with oxygen will not be reliable.[1]

Grist.

In the case of gunpowder it is necessary to grind the ingredients very finely, and mix them intimately, to obtain the best results, but when one or more of the constituents is explosive by itself, coarser grinding and rougher mixing suffice. In the case of "safety" explosives for coal mines it is often considered inadvisable to grind some of the ingredients too finely, as it appears to increase the tendency to ignite gas and coal dust. When an explosive contains a small proportion of nitro-glycerine to render it easier to detonate, this liquid should not be so thoroughly absorbed and incorporated that its liquid character is entirely destroyed, but it must be retained so well that there is no tendency to exudation. Therefore the wood-meal, that these explosives often contain, should not be too fine. Each explosive requires separate study to ascertain the best conditions of grinding and mixing.

From the point of view of manufacture it is important that an explosive should be of such a nature that it is easily dealt with in the machines for loading it into cartridges. It is most convenient if it be either pasty or gelatinous, or a free running powder. It is apparently with the object of obtaining a powder of better physical properties that many explosives are made with starch or flour instead of, or in addition to, wood-meal.

English Statistics.

The following Table gives the quantities of different explosives that were used in Great Britain and Ireland in coal and metalliferous mines and in quarries under the Quarries Act in 1912:

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[1] *See* Spielmann, *Zschft. Steinbruch-Berufs-Gen.* through *S.S.*, 1915, p. 104. L. Sieder, *S.S.*, 1915, pp. 165 and 179. *Also S.S.*, 1915, p. 186.

	Quantity used lbs.	Percentage
Permitted explosives	9,361,698	31·7
Gunpowder	15.494.935	51·4
Gelignite	3.583.516	11·9
Gelatine dynamite	447,769	1·1
M.B. powder	431,375	1·1
Blasting gelatine	258,982	0·9
Blastine	176,592	0·6
Polarite	144,162	0·5
Cheddite	114.021	0·4
Saxonite	81,623	0·3
Steelite	18,598	0·1
Dynamite	14.838	
Oakley Quarry Powder	5.400	
Tonite	728	
Preposite	20	
	30.134,257	100·0

In 1913 the quantities were

	Quantity used lbs.	Percentage
Permitted explosives	11.051.231	33·0
Gunpowder	17,060,874	50·1
Gelignite	3.960.173	12·0
Gelatine dynamite	474,922	1·4
Blasting gelatine	297,907	0·9
Roslin Giant Powder	247.871	0·7
Cheddite	187.226	0·6
Nobel Polarite	149.593	0·5
Blastine	122,590	0·4
Saxonite	85,606	0·3
Dynamite	13,010	0·1
Stonax	7.937	
Matagnite gelatine	3,000	
	33.661.940	100·0

And in 1914:

	Quantity used lbs.	Percentage	Used Principally for
Gunpowder	16,051,879	49·5	All purposes
Permitted explosives	8.724,866	26·9	Coal mines
Samsonite	403,015	1·2	..
Saxonite	129,608	0·4	,,
Ammonal	327,850	1·0	Quarries
Ammonite	108.030	0·3	Coal mines
Rippite	208,331	0·7	..
Arkite	195.843	0·6	..
Stowite	123,290	0·4	..
Swalite	137.622	0·4	..
Others on old Permitted List	3,699.841	2·2	..

	Quantity used lbs.	Percentage	Used Principally for
Gelignite	3,926,140	12·2	All purposes
Modified gelignites	84,463	0·3	Metal mines
Gelatine dynamite	390,576	1·2	,,
Blasting gelatine	309,393	0·9	Quarries
Cheddite	184,525	0·6	Coal and quarries
Nobel Polarite	193,136	0·6	Quarries
Blastine	142,521	0·5	,,
Blasting Bellite	22,837	0·1	,,
Dynamite	12,201		,,
Ergites	10,100		,,
Sabulite	2,324		Metal mines
Tonite	1,978		Quarries
Oakley Quarry Powder	1,825		,,
Steelite	990		,,
	32,393,184	100·0	

American Statistics.

According to a bulletin of the Census Bureau of the United States the following quantities of explosives were produced there in 1909:

	Millions of pounds	Price cents per pound
Dynamite	195	11
Blasting powder	233	4
Nitro-glycerine	29	11
Gunpowder	13	14
Permissible explosives	10	9
Smokeless powder	6	68
Gun-cotton, etc.	1	
	487	

In 1912 the consumption in millions of pounds was:

	Coal-mines	Other mines	Railways and other constructions	All other uses	Totals
Gunpowder	187·1		18·5	24·7	230·3
High explosives (non-permissible)	20·9	89·7		123·9	234·5
Permissible explosives	18·1	4·7		1·8	24·6
Totals	226·1	94·4	18·5	150·4	489·4

In 1913 the production was:

Black blasting powder	194	million lb.
High explosives (non-permissible)	242	,,
Permissible explosives	28	,,
	464	,,

And in 1914:

Black powder	206	million lb.
High explosives (non-permissible)	218	,,
Permissible explosives	26	,,
	450	,,

In 1913 the consumption was:

	Coal-mines	Other mines	Railways and other constructions	All other uses	Totals
Gunpowder	184·9	8·3	15·7	21·0	229·9
High explosives (non-permissible)	24·1	92·1	33·2	93·0	242·4
Permissible explosives	21·8	4·7	0·4	0·7	27·7
Totals	230·8	105·1	49·3	114·7	499·9

And in 1914:

	Coal-mines	Other mines	Railways and other constructions	All other uses	Total
Gunpowder	176·8	7·6	7·9	13·8	206·1
High explosives (non-permissible)	24·2	84·3	28·0	82·0	218·5
Permissible explosives	19·6	4·8	0·3	1·0	25·7
Totals	220·6	96·7	36·2	96·8	450·3

Products from Explosives

Carbon monoxide.

Some of the products formed by explosives are poisonous, notably carbon monoxide, which is produced in considerable proportion whenever the oxygen in the explosive is insufficient to convert all the carbon into dioxide and the hydrogen into water. The gases from black powder of standard composition contain from 8 to 17 per cent. of carbon monoxide by volume, but if the percentage of saltpetre be less than 75, of course there is more. Blasting gelatine contains just about enough oxygen for complete combustion, whereas British gelatine dynamites and gelignites usually have a slight excess. Ammonium nitrate explosives often contain a considerable excess of oxygen, but they vary very much in this respect, and some are deficient in this constituent. Many of the explosives used in coal-mines give more carbon monoxide than dioxide. As a rule the ventilation is so good that no evil consequences result, but this is not always the case. In the days when black powder only was used, mine sickness was a frequent complaint and was due to poisoning with carbon monoxide. In 1904 in a mine at Grängesberg two miners were found dead, presumably from this cause,[1] and in 1908, when an underground magazine exploded in a coal-mine in West-Essen, five men were fatally poisoned by the gas formed, in addition to six killed directly by the explosion. In the South African gold-mines the miners suffer much from what is generally called "miners' phthisis," and in 1902–1903 a Royal Commission inquired into the matter and found that it was due principally to carbon monoxide, which was found to be present in mine air. The explosives used contain sufficient oxygen for their complete oxidation, but it has been shown by Weiskopf [2] that the formation of the monoxide is due to the paper in which the cartridges are wrapped.[3] Mann carried out numerous experiments in the gold-mines of Western Australia,[4] and in samples of air taken as soon as possible after firing the charges he always found carbon monoxide, in some cases, where a number of holes were fired simultaneously, there was over 1 per cent. In the trials with blasting gelatine, gelatine dynamite and gelignite, from a seventh to a seventeenth of the carbon appeared as monoxide, the mean being a twelfth. When the diameter of the cartridges was increased there was less carbon monoxide, and when the wrappers were removed the proportion was reduced to about a fiftieth. Similar results have been obtained by C. Hall and S. P. Howell with American explosives.[5] Increasing the proportion of oxygen in the explosives was not very effective, neither was the use of special "anti-fume" composition: and as it is not desirable to remove the wrappers in ordinary work, the only really satisfactory way to prevent injury to the miners is to have very good ventilation, and to prevent them approaching the working face until the fumes have had time to dissipate. The safety fuse also produces a considerable amount of carbon monoxide, but this source of

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[1] Nauckhoff, *S.S.*, 1909, p. 241.

[2] *J. Chem. Met. and Min. Soc. of S. Africa*, 1909, p. 258; *S.S.*, 1909, p. 352.

[3] *See also* Moir, *J. Chem. Met. and Min. Soc. of S. Africa*, vol. iv., p. 46.

[4] *Report to W.A. Parliament*, 1911.

[5] *U.S. Bureau of Mines Bulletin*, No. 48, 1913, p. 16.

trouble may be avoided by the use of electric detonators. If the material that is blasted be of a reducing character, such as coal or sulphide ore, it is inevitable that much monoxide will be produced, whatever measures be taken. Heise states [1] that between 1895 and 1898 there were ten fatal cases of poisoning with carbon monoxide in German coal-mines, although the dynamite used always contained an excess of oxygen.

The highly poisonous character of carbon monoxide is due to the fact that its affinity for the hæmoglobin of the blood is about 250 times that of oxygen. Consequently, when a man works in an atmosphere contaminated with the gas, his blood gradually becomes more and more inactive, and it only regains its full power of supporting life many hours after the man has returned to a normal atmosphere. If the amount of the gas exceed 0·02 per cent., symptoms of poisoning will appear when a man has been working for some hours. Up to 0·05 or 0·1 per cent. a man can bear it without serious inconvenience for a half to one hour, whereas in the same space of time 0·2 to 0·3 per cent. is dangerous to life. It can be detected in air by the decolorizing effect it has on palladium chloride solution : as little as 0·04 can be detected with certainty by this method.[2] Its poisonous action on small birds, such as canaries, can also be utilized : 0·25 per cent. affects a bird in one minute, and in three minutes makes it fall from its perch.[3] It is best estimated by the quantity of iodine set free from heated iodine pentoxide.[4] For the cure of cases of poisoning of this kind, inhalation of oxygen is the only effective measure.

The high explosives mostly used for military demolitions, gun-cotton, picric acid and trinitro-toluene, form large quantities of carbon monoxide when detonated. Hence they are very unsuitable for use in underground workings unless mixed with a considerable proportion of an oxygen carrier.

The following percentages of carbon monoxide and dioxide were found by L. Lewin and O. Poppenberg [5] in the gases obtained when the explosives were exploded in a bomb, presumably at low density of loading :

	CO	CO_2	
Nitro-cellulose powder	46·9	16·8	per cent.
Dynamite	0	—	
Gelignite	34·0	32·7	,,
Carbonite	36·0	19·2	,,
Picric acid	61·0	13·5	,,
Trinitro-toluene	57·0	1·9	,,
Ammonal	23·7	6·1	,,

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[1] *Glückauf*, 1899, p. 341.

[2] *See* Nauckhoff, *S.S.*, 1909, p. 241.

[3] Burrell, *U.S. Bureau of Mines Technical Paper* 11.

[4] This method was invented in France in 1898, and was used by J. Moir in South Africa, 1902. *See J. Chem. Met. and Min. Soc. of S. Africa*, May, 1915.

[5] *S.S.*, 1910, p. 4.

The percentage of carbon monoxide depends not only on the composition of the explosive but also, in the case of substances such as picric acid and trinitrotoluene, on the conditions under which they are fired. The amount of carbon monoxide is considerably smaller when the explosive is doing work, that is under the conditions of actual use.[1]

Nitrogen oxides.

When properly detonated practically all the nitrogen in ordinary explosives is liberated in the elementary state, but those that contain a large excess of oxidizable substances generally give some ammonia as well. Very little oxide of nitrogen is formed even by highly oxidized explosives: Mann estimated that in the air immediately after firing shots there was on an average 0·0047 per cent. NO_2; the greatest quantity he found was 0·025 per cent. These quantities are of minor importance compared with those of the carbon monoxide. But when explosives burn, most of the nitrogen is liberated as nitric oxide NO, and this is converted by the air into the peroxide NO_2, and the same occurs to a great extent in the case of a blown-out shot. Hence with these there is danger of poisoning with nitrous fumes. A blown-out shot should therefore never be approached too soon. The smell of the nitrous fumes is always perceptible, but the danger of the nitric peroxide lies in the fact that its full effects appear only some hours after inhalation. There are many cases on record of men going home apparently quite recovered from the effects, and then dying in convulsions in the night. As a cure doses of chloroform water were formerly much recommended,[2] but Curschmann, after investigating the matter, came to the conclusion that chloroform is no good, and may be injurious. Inhalation of oxygen he considers to be the only effective measure,[3] and this is the method generally recommended now. The patient should also have an emetic administered, such as a warm 10 per cent. solution of salt, until he is sick. As a protection against the gas a gas-mask may be used such as are worn in the trenches, or, failing this, a wet cloth or handkerchief covering the mouth and nostrils, but it is better to moisten it with a solution consisting of washing soda 80 parts, glycerine 15 parts, and water 100 parts. This solution is also effective against most of the other poisonous gases that are liable to be given off by explosives such as prussic acid, hydrochloric acid and hydrogen sulphide, but not against carbon monoxide. Cases of gassing with nitrous fumes are also liable to occur in the manufacture of nitro-compounds and nitric ethers: when they do, the same measures should be adopted.

Acrolein, prussic acid nitro-glycerine.

Blown-out shots are liable to produce other poisonous gases and vapours, such as acrolein and prussic acid. Nitro-glycerine explosives distil off part of this constituent, which condenses again to a fine mist in the air: if a sweet taste be observed in the air, the miner should leave at once and not return

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[1] *See* O. Poppenberg and E. Stephan, *S.S.*, 1910, p. 294. [2] *A.R.*, 1904, App. V.

[3] *Deutsche Medizinische Wochenschrift*, 1911, No. 22; *S.S.*, 1911, p. 418. But *see also P. et S.*, vol. xvi., p. 200.

until it has disappeared.[1] Sarrau and Vieille found that potassium cyanide is a normal product of the explosion of potassium picrate.[2]

Hydrochloric acid.

Ammonium perchlorate explosives, such as Blastine, form hydrochloric acid. This is about ten times as poisonous as carbon monoxide, but probably is not so dangerous as its presence cannot escape notice.

Hydrogen sulphide.

Black gunpowder and other explosives containing sulphur yield a considerable proportion of hydrogen sulphide (sulphuretted hydrogen) when they explode. This unpleasant and poisonous gas is therefore amongst the products of many American dynamites. The following Table shows the products obtained when various American explosives[3] were fired in a Bichel pressure gauge. A charge of 200 g. in its original wrapper was used in each test, except with black blasting powder of which 300 g. were used.

COMBUSTION PRODUCTS RESULTING FROM TESTS OF EXPLOSIVES IN THIN PARAFFINED PAPER WRAPPERS

(A. L. Hyde, analyst, *U.S. Bureau of Mines Bulletin*, No. 48, p. 10)

Class and grade of explosives	Electric detonator used, No.	Weight of products of combustion (grammes)			Gaseous products (per cent. by volume)							Solids (per cent.)		Volume of gas (litres)
		Gaseous	Solid	Liquid	Carbon dioxide	Carbon monoxide	Oxygen	Hydrogen	Methane	Nitrogen	Hydrogen sulphide	Soluble	Insoluble	
30 per cent. "straight" nitro-glycerine dynamite	6	96·8	102·1	12·9	22·9	28·4	0·0	20·6	0·7	27·4	—	88·00	12·00	85·8
40 per cent. "straight" nitro-glycerine dynamite	6	107·4	87·1	12·4	27·3	26·9	·0	18·0	·4	27·4	—	86·73	13·27	88·5
50 per cent. "straight" nitro-glycerine dynamite	6	124·6	70·3	14·7	24·4	31·2	·0	20·7	·7	23·0	—	79·14	20·86	105·5
60 per cent. "straight" nitro-glycerine dynamite	6	143·5	49·6	11·9	22·2	34·6	·0	23·2	·8	19·2	—	68·53	31·47	128·9
60 per cent. strength low-freezing dynamite	6	161·5	43·5	3·9	8·9	47·4	·0	31·0	·6	12·1	—	78·76	21·24	169·5
40 per cent. strength ammonia dynamite	6	95·7	85·9	26·1	41·4	3·8	·0	3·1	·8	45·5	5·4	86·03	13·97	65·6
40 per cent. strength gelatine dynamite	6	96·3	96·3	11·7	50·8	3·0	·0	1·8	·8	39·5	4·1	87·32	12·68	60·3
5 per cent. granulated nitro-glycerine powder[4]	6	115·5	93·6	8·[illegible]	51·3	2·7	·0	·9	·7	28·7	15·7	78·00	22·00	61·6
FFF black blasting powder	(5)	154·4	126·9	4·1	49·7	10·8	·0	1·8	·6	28·4	8·7	91·20	8·80	67·8

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[1] *See* Jakobj and His, *S.S.*, 1907, p. 261.

[2] *P. et S.*, vol. ii., p. 151.

[3] The explosives named in this Table are not of the same formulae as those in the Tables on pp. 362 and 373.

[4] Primer of 40 per cent. "straight" nitro-glycerine dynamite, representing 10 per cent. by weight of the charge, was used, but the gases evolved by the dynamite were deducted in the computations of the volume of gas.

[5] Black-powder igniter used.

Stemming.

The question as to the best methods of stemming shots has been examined experimentally by W. O. Snelling and C. Hall,[1] who fired charges of 10 grammes of explosives stemmed with varying quantities of sand and fire-clay in Trauzl lead blocks provided with an extension of the bore-hole. It was found that the increase in efficiency from the use of stemming varies considerably with different explosives. When they are slow burning, like black blasting powder, a large quantity of stemming is required for effective results, and the greater the quantity of stemming used, and the more firmly this stemming is tamped into the bore-hole, the greater is the useful work done by the shot. With 40 per cent. "straight" dynamite, which is very quick acting, and with 40 per cent. ammonia dynamite, which is intermediate between this and slow burning explosives, small quantities of stemming greatly increase the efficiency, and further additions raise it higher, but at a diminishing rate. With 200 grammes of stemming the following enlargements were obtained:

	Gun-powder	Ammonia dynamite	Straight dynamite
Untamped dry sand	56	446	642
Untamped dry fire-clay	57	378	589
Tamped dry sand	53	417	612
Tamped dry fire-clay	57	381	635
Tamped moist sand	71	470	696
Tamped moist fire-clay	19	487	710

Under practical conditions gunpowder, like the other explosives, gives the best results with moist fire-clay.

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[1] *U.S. Bureau of Mines Technical Paper*, No. 17.

CHAPTER XXXV

COAL-MINE EXPLOSIVES

Nomenclature : Coal-mine explosions : Testing galleries : In France : In Austria : In Germany : In Belgium : In England : In America : Different systems of testing : Explosive atmospheres : Coal-dust : Influence of size of bore : Dimensions of gallery : Incomplete decomposition : Flames : Effect of alkali salts : Effect of density : Incorporation : Wrappers : Length of the cannon : Stemming : Failure to detonate : Conclusions : Classification : Hydrated explosives.

Nomenclature. EXPLOSIVES specially intended for use in coal-mines are often called "safety explosives," but objections have been raised to the term on the ground that it is the duty of an explosive to explode, and that therefore it cannot be safe under all circumstances, and that the use of this expression may lead to carelessness in dealing with these materials. Also it has been contended that the use of the term should be confined to those explosives which are comparatively insensitive to blows and friction, such as ammonium nitrate explosives containing no nitro-glycerine. In German, distinction is drawn between those that are safe in handling (handhabungssichere) and those that are safe for use in coal-mines (schlagwettersichere), and in French it has been proposed to confine the use of the expression "explosifs de sûreté" to the former class, and to call the explosives for dangerous coal-mines "explosifs antigrisouteux." Nevertheless, what is generally understood by a safety explosive is one that has been officially tested and found to be comparatively safe when exploded in the presence of fire-damp (methane). Officially the explosives that are allowed to be used in dangerous coal-mines in Great Britain are termed "Permitted Explosives." In the United States of America they are called "Permissible Explosives." In this work, which deals with explosives in all countries, preference has been given to the more general name, "coal-mine explosives."

Coal-mine explosions. In order to prevent mine explosions three important precautions are generally taken: the use of safety lamps, efficient ventilation of the workings, and the employment of explosives that are not liable to ignite fire-damp. The development of safety explosives and the methods of testing them were briefly reviewed in Chapter III. As the depth and extent of mines has been increased, ventilation has become more and more essential, not only to remove any gas that may escape from the coal, but also to provide a healthy atmosphere for the miners; but this has greatly increased another source of danger, namely, that from coal-dust. The large volume of air, heated by compression, streaming through the galleries dries the dust produced by the tramping of the men and horses, and this dust is capable of forming an explosive mixture with air. Although not so easily ignited as a mixture of methane and air, it is quite as dangerous, because coal-dust explosions are generally far more extensive. In December, 1907, three explosions occurred in the Pennsylvania coal-field, and in each case practically every man in the mine was killed; the death-roll amounted to 633. In the mine explosion at Courrières, in the North of France, in 1905, about 1100 men lost their lives. There have also been explosions in England and Germany in which several hundred men have been killed. In all these cases the vast extent of the catastrophes is ascribed to the presence of coal-dust. With efficient ventilation it is not possible for fire-damp to be present in explosive proportion except in small isolated localities, but the presence of more or less coal-dust cannot be avoided anywhere. The initial ignition is in many cases probably due to fire-damp, but the explosion is propagated and extended by the dust. The explosive wave is preceded by a rush of air which stirs up the dust and so prepares the way for the explosion. Some sorts of coal give dust which is more dangerous than that from others. Fineness of the dust, a large proportion of volatile matter, and evolution of gas at a low temperature, are factors tending to favour explosion. At the testing stations safety explosives are now tested as to their liability to ignite mixtures of coal-dust with air, or with air and inflammable gas. As a general rule the results obtained are much the same as with mixtures of air and inflammable gas only, but some explosives of the ammonium nitrate class ignite coal-dust more readily than they do gas. Other measures have also been tried for diminishing the danger from coal-dust: watering the roads and galleries in order to lay the dust throughout a mine and make it uninflammable is unfortunately impracticable, although it can generally be adopted in the immediate vicinity of the place where a shot is to be fired. In short testing galleries it is not possible to reproduce the effects that have been observed at Courrières and elsewhere, but at Altofts in England a gallery 200 metres long has been erected, resembling in section as nearly as possible that of a coal-mine. At Liévin in France also there is a gallery 230 metres long for the study of these questions, and recently experiments have been carried out in an old mine gallery at Commentry. From trials in these it has been found that in a dusty mine the explosive wave gradually increases in velocity as it proceeds, until it may exceed 1000 metres per second. Such violent waves can be extinguished by placing much fine stone-dust or ash in the gallery. The incombustible dust must be at least equal in amount to the coal-dust present, and may with advantage be placed on supports across the gallery near the roof. There should be at least 400 litres of stone-dust or ash per cubic metre of gallery, extending over a length of 10 to 20 metres. It has been found by Taffanel that sharp corners in the gallery slow down a coal-dust explosion, and may stop it altogether. Slow explosive waves are better extinguished by another device, also used by Taffanel: a number of troughs, semicircular in section, filled with water and placed across the roof of the gallery. There should be 120 litres of water per cubic metre for a length of not less than 10 metres.[1] It has also been suggested by Harger that the air in a mine could be rendered incapable of forming explosive mixtures by slightly diminishing the percentage of oxygen in it, but this theory is not generally accepted, and it is contended that the experimental facts do not bear out Harger's statements.

Testing galleries. In all the principal countries of Europe, possessing coal mines, testing galleries have been erected, in which safety explosives can be tested by firing them into an explosive atmosphere.

France. In France a testing station has been built at Liévin by the coal owners of the Pas de Calais. There is a small gallery 2 square metres in section and 15 metres long for the study of explosives, and a large one 2·8 square metres in section and 230 metres long for the study of coal dust explosions, etc. The selection of explosives for use in French coal-mines was until recently based on theoretical considerations; the following two conditions had to be satisfied:

(1) Their products of detonation must contain no combustible constituent, such as hydrogen, carbon monoxide, solid carbon, etc.

(2) Their temperature of detonation, calculated in the prescribed manner, must not exceed 1900° for explosives used for penetrating rock, nor 1500° for work in the coal-seams.

Austria. In Austria shots are fired freely exposed in a mixture of fire-damp and air. The manufacture of explosives is, however, a State monopoly, and for the comparatively unimportant Austrian coal-mines the only explosives permitted are Dynammon and Wetter-dynammon.

Germany. In Germany the law prescribes that only safety explosives may be used in mines in which fire damp or inflammable coal-dust has been found. The onus of proof that an explosive is safe rests with the mine owners, and testing stations have been erected by the Mine Owners Association at Gelsenkirchen and Grube Maria. A number of the explosives factories also possess testing galleries for their own use: such galleries exist at Haltern, Schlebusch, and Castrop. The gallery at Gelsenkirchen may be taken as typical of a whole class; it is 34 metres long and elliptical in section with the major axis vertical; the diameters are respectively 1·80 and 1·35 metres. The charge of explosive is fired without stemming from a cannon with a bore 4 cm. in diameter and 70 cm. deep. This is fixed at one end of the gallery and inclined so that a prolongation of the bore would strike the roof of the gallery about 10 metres

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[1] *See* Vennin et Chesneau, pp. 537–560.

from the farther end, in order to imitate more closely the condition of an actual shot in a mine. At the end where the gun is, an explosion chamber of 10 cubic metres capacity is formed by means of a paper diaphragm.

Belgium.

Although the testing of explosives has only been taken up in Belgium comparatively recently, the work done at the testing station at Frameries by Watteyne and Stassart has advanced the matter considerably. The gallery is similar to the one at Gelsenkirchen, 30 metres long and elliptical in section; axes 1·40 and 1·85 metres, sectional area 2·0 square metres. The bore of the gun is 5·5 cm. in diameter and 46 cm. long; it is inclined upwards, and is fired without stemming into an explosion chamber 10 cubic metres in capacity, as at Gelsenkirchen. The explosive atmosphere contains 8 per cent. of purified fire damp, and is warmed to a temperature of 25°. Tests are also carried out with mixtures of coal dust and air. A charge is first fired, which is large enough to cause ignition, and then it is gradually diminished, 50 g. at a time, until one is found which in ten shots causes no ignition. The tests are then repeated in the presence of coal-dust. The maximum charge that can be fired without causing ignition is called the "charge limite." Tests are also carried out in the Trauzl block to ascertain the charge equal in strength to 10 g. of Dynamite No. 1. If the "charge limite" is equivalent to more than 175 g. of dynamite, the explosive is placed on the list of "Explosifs S.G.P." (Sûr-Grisou Poussières).

England.

The testing gallery erected at Woolwich consisted of a comparatively small iron tube 27·5 feet (8·4 m.) long and 2·5 feet (0·76 m.) in diameter, circular in section. The bore of the gun was 30 inches (76 cm.) long and $1\frac{7}{8}$ inches (4·8 cm.) in diameter; its axis was parallel with that of the gallery. The strength of the explosive to be tested was first ascertained by firing it into the ballistic pendulum, and then charges of a certain strength were fired stemmed with a fixed amount of dry clay into a mixture of 15 per cent. coal-gas and 85 per cent. air. The details of the test were altered from time to time. The smaller sectional area of the Woolwich gallery rendered the test much more sensitive, and the gas mixture employed was also more easily ignited than those used on the Continent; but, on the other hand, the use of stemming enabled many explosives to pass which otherwise could not have done so. One of the most remarkable effects of the differences in the tests was that a non-detonating explosive, Bobbinite, was successful in getting placed on the "Permitted List." This has been very popular with miners, as no detonator is required to fire it, and it does not break up the coal so much as a more violent explosive. It caused a number of ignitions, without, however, doing any very serious damage, and in consequence of these a Departmental Committee was appointed in 1906 to inquire whether non-detonating explosives should not be excluded entirely from coal-mines. The Committee did not recommend the total exclusion of Bobbinite and similar explosives, but suggested the adoption of a supplementary test on the same lines as that applied at Frameries, and that for operations in mines where there is danger of a widespread explosion of coal-dust only those explosives should be used which gave a high "charge limite" when fired unstemmed.

A larger testing gallery has now been erected at Rotherham. This is 50 feet (15·2 m.) long and 5 feet (1·52 m.) in diameter; it is circular in section and constructed of iron. The explosion chamber has a capacity of 10 cubic metres. The gun has a bore 2 inches (5·1 cm.) in diameter and 4 feet (122 cm.) long. The cartridges have a diameter of 1⅔ inches (3·2 cm.). Shots are fired unstemmed into a mixture of air with 13·5 per cent. coal-gas, until the largest charge is found which can be fired without igniting the mixture. Further shots are fired, beginning with this charge and, in the event of an ignition, reducing the charge until five shots of the same weight have been fired without igniting the mixture. Shots are then fired into a mixture of coal dust and air. The lower of the charges thus determined is known as the "Maximum Charge."

Charges of 4 ounces are also fired at the ballistic pendulum, and the swing obtained is compared with that given by 4 ounces of gelignite containing 60 per cent. of nitro-glycerine.

The Explosives in Coal-Mines Order of March 31, 1913, gave the first list, containing twenty different explosives, which had passed this test, but it was provided that those on the previous list, which had passed the Woolwich test, should still be permitted until December 31, 1913. By the Order of September 1, 1913, the use of Bobbinite has been restricted to mines that are not dangerous on account of either gas or coal-dust. With this exception the old list has been abolished. Up to May 13, 1914, forty-six explosives had passed the Rotherham test. The more severe conditions of the Rotherham test have rendered it necessary to dilute the explosives with such substances as sodium chloride, ammonium chloride and ammonium oxalate. Grave doubts have been expressed whether the explosives thus produced are really safer than those formerly used, which had passed the Woolwich test.

America.

In the United States legislation as regards the use of explosives in coal-mines is in the hands of the individual States. Nevertheless, a testing gallery has been erected at Pittsburg under the charge of the Bureau of Mines of the Central Government (*see* Figs. 129, 130). Here explosives are tested, and as there is no power to order what shall be used, those that are successful in passing the tests are merely placed on a list of "Permissible Explosives." The gallery is circular in section and made of boiler plate: it is somewhat larger than other galleries, having a diameter of 6 feet 4 inches (1·93 m.) and a length of 100 feet (30·5 m.). The bore of the cannon is 2¼ inches (5·72 cm.) in diameter and 21½ inches (54·6 m.) deep. The explosive gas mixtures are made with natural gas containing about 82 per cent. methane, 16·4 per cent. ethane, and 1·5 per cent. nitrogen; tests are also carried out with bituminous coal-dust, ground to pass a 100-mesh sieve. Shots are first fired at the ballistic pendulum to ascertain the charge equivalent to 8 ounces (227 gr.) of standard 40 per cent. American dynamite. Series of ten shots of the equivalent charge are then fired into (1) a mixture of gas and air containing 8 per cent. of methane and ethane; (2) a mixture containing 4 per cent. methane and ethane and 20 lb. of coal-dust, and (3) air with 40 lb. of coal-dust only. In each of these tests the equivalent charge is taken and is tamped with 1 lb. of dry clay; the gallery is maintained at a temperature of 77° F. (25° C.). Shots are also fired unstemmed into mixtures of air and 20 lb. coal-dust with 4 and 2 per cent. gas respectively with the object of establishing a limit charge, but as this mixture is somewhat insensitive to ignition by most explosives, all the successful explosives failed to ignite with a charge of 1½ lb. (680 g.). Some English explosives, which had passed the Woolwich test, gave only very small limit

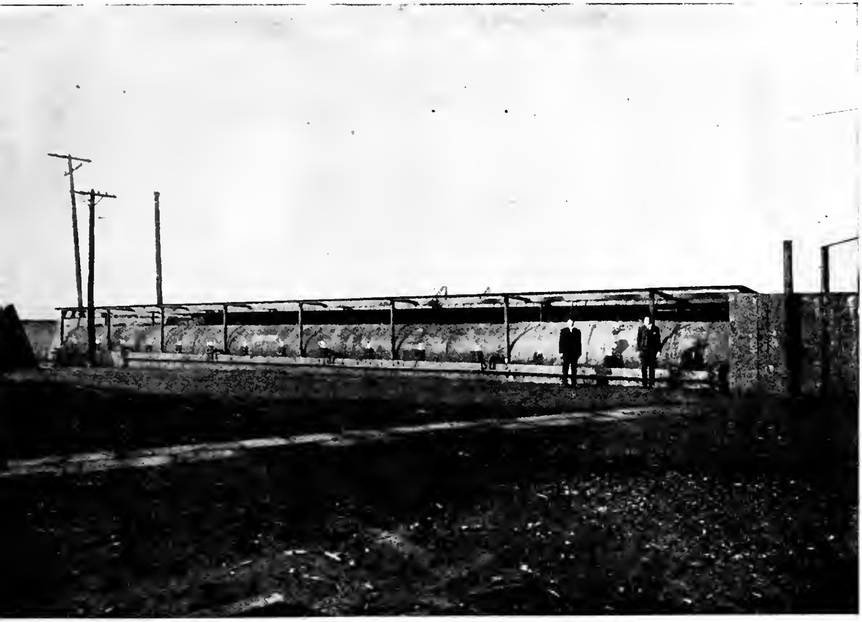

FIG. 129. United States Testing Gallery, Pittsburg, Pennsylvania

charges, however. If the equivalent charge be 1 lb. or more, the explosive is not placed on the Permissible List, for such explosives do not break down the coal satisfactorily unless they are used in charges of more than 1½ lb., and such large charges are believed to be dangerous in gassy and dusty mines. A number of other properties of the explosives are observed at the Pittsburg testing station, including: density, Trauzl test, velocity of detonation, height and duration of flame, falling weight test, explosion by influence, pressure developed, heat evolved, and compression of small lead blocks. All explosives that produce 5½ cubic feet (158 litres) of carbon monoxide or other poisonous gas from a 1½ lb. charge are removed from the Permissible List. The explosives should show no diminution in sensitiveness to detonation in 6 months. The results of all these tests on a considerable number of American safety explosives are given in *Bulletins* 15 and 66, but the compositions of the explosives are not stated.

Fig. 130. Explosion of Dust and Gas in United States Testing Gallery

There are three fundamentally different methods of firing explosive charges in testing stations: (1) freely exposed as in Austria; (2) from a cannon without stemming, and (3) from a cannon with stemming. None of these represents at all closely the conditions of a normal blasting shot fired in a coal-seam, but this is not required, because it is recognized that it is the abnormal shots that constitute the greatest danger. The Woolwich test represented approximately the conditions of a "blown-out shot," such as is obtained when the bore hole is overcharged or insufficiently tamped. Hang-fires and blown-out shots are sources of considerable danger in coal-mines. They may be caused by the bursting of cartridges during the loading of the bore-hole, and the consequent admixture of coal-dust with the explosive.[1] Sometimes a bore-hole traverses or passes near to a fissure in the coal containing fire-damp, and it has been found that explosives which have passed the Woolwich test are liable to ignite the gas when this is the case. An unstemmed shot represents this condition of affairs more nearly, and it is principally for this reason that this system of testing is now adopted so generally. The Austrian test imitates what would happen if a miner accidentally exploded a cartridge which had not been placed in a bore-hole at all, but this is an occurrence which should be very rare, and the general adoption of this test in countries which have extensive coal-mines would hamper the industry too much. The results obtained depend not only on the nature of the explosive that is tested, but also on the dimensions of the gallery and of the cannon, and on the composition, temperature and pressure of the explosive gas mixture used.

Different systems.

The explosive atmosphere of the testing gallery is generally made by mixing either coal-gas or fire-damp (pit gas, methane) with air. Fire-damp is the more satisfactory, as it is the gas which actually occurs in the mines, but there are few localities where there is a sufficient and uniform supply of it available; it is liable to be mixed with varying proportions of air and other impurities. It is, therefore, found necessary to purify the gas before use and to analyse the explosive mixture each time. Synthetic methane is unfortunately too expensive to use in the very large quantities that are required for these tests. At Rotherham and some other stations coal gas is used, as it is always available. Its mixtures with air are, however, more liable to explode than those of methane, because in addition to methane it contains considerable proportions of hydrogen and carbon monoxide. In all these gaseous mixtures there is an upper limit of explosibility as well as a lower one, and if the proportion of inflammable gas be raised above it, the mixture may burn but will not explode. These explosive limits have been determined

Explosive atmospheres.

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[1] *See* Dautriche, *P. et S.*, vol. xiv., p. 5. Also Watteyne and Lemaire, *Ann. des Mines de Belgique*, 1913, pp. 781–810.

by both Kubierschky[1] and Bunte,[2] and by a number of others.[3] The results depend upon the conditions under which the tests are carried out.

	Explosive limits	
	Kubierschky	Bunte
	Per cent.	Per cent.
Methane	6·0–12·0	6·1–12·8
Hydrogen	9·5–64·7	9·5–66·4
Carbon monoxide	14·3–74·6	16·5–75·0
Coal gas	7·0–22·6	7·9–19·1

There is also a considerable difference in the temperatures at which the different gases are ignited. These temperatures also depend upon the conditions of the experiment. Dixon and Coward[4] found the following:

Methane	650–750°
Hydrogen	580–590°
Carbon monoxide	640–660°
Ethane	560–630°

In the case of methane, and to a smaller extent ethane and other hydrocarbons, the time during which the gases are exposed to the high temperature and the nature and extent of the heating surface produce much more effect than in the case of hydrogen or carbon monoxide. This is doubtless due to the fact that the hydrocarbons are first converted into aldehydes, which are then further oxidized, as has been shown by Bone and Wheeler. It is not to be expected, therefore, that explosives differing very much as to the temperature and composition of their products will give comparable results when tested in two different testing stations, if in the one case methane is used and in the other coal-gas. This may be urged as an objection to the use of coal-gas in testing galleries. Moreover, coal-gas is liable to vary considerably in composition, and if it contain water-gas the results may be quite different.

Will[5] carried out experiments in a miniature gallery using different inflammable gases, and found the following limit charges:

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[1] *Ang.*, 1901, p. 130.

[2] *J. f. Gasbel.*, 1901, p. 835.

[3] Eitner, *J. f. Gasbel.*, 45, p. 21. N. Teclu, *J. pr. Chem.*, 75, 1907, p. 212. Burgess and Wheeler, *Proc. Chem. Soc.*, 1911, p. 262; *Trans. Chem. Soc.*, 1914, p. 2591. Burrell and Boyd, *J. Ind. Eng. Chem.*, 1915, p. 414. *U.S. Bureau of Mines Technical Paper*, No. 119. S. G. Sastry, *Trans. Chem. Soc.*, 1916, p. 523.

[4] *Trans. Chem. Soc.*, 1909, pp. 514–543. *See also* Dixon and others, *Trans. Chem. Soc.*, 1914, pp. 2027, 2037.

[5] *S.S.*, 1909, p. 326.

	9·8 per cent. Coal-gas	9 per cent. Methane	2·8 per cent. Petroleum ether	24·5 per cent. Coal-gas
	Grammes	Grammes	Grammes	Grammes
Trinitro-toluene	4	8	9	12
Astralite	5	8	8	10
Wetter-Astralite	10	12	12	14
Strengthened Chrom-Ammonite	10	20	13	13
Ammon-Carbonite	25	25	25	25
Gelatine Wetter-Astralite	50	35	30	30
Chrom-Ammonite 1908	65	40	35	35

Although the explosives in every case fall into the same order, the differences with the various gases are considerable. The proportion of methane used at the testing stations is 8 to 9 per cent., which mixture has the greatest degree of sensitiveness. At Rotherham a mixture of 13·5 per cent. coal-gas with 86·5 per cent. air is used, which is the most sensitive mixture of this gas. By using a smaller proportion of gas, a mixture would be obtained with a lower degree of sensitiveness, more nearly approaching that of the methane-air mixtures, but with such mixtures slight variations in the proportions make a considerable difference in the sensitiveness, and this is not the case with the mixture of maximum sensitiveness.

The fact that at low temperatures there is a considerable retardation in the ignition of methane was pointed out many years ago by Mallard : at 650° he estimated that 10 seconds were required to effect ignition. It is upon this observation that the French official rule which limited the temperature of explosion of explosives was founded, for it was considered that, before the retardation interval expired, the temperature of the products of explosion would be reduced below the ignition point of the explosive atmosphere, provided that the temperature of explosion of the explosive was below 1500°.

Coal-dust.

Tests are now carried out with coal-dust as well as with gas mixtures. The results obtained depend upon the composition and quantity of the dust. In order that the conditions may be as uniform as possible the coal should be freshly ground and sifted. The ease of ignition of the dust depends upon the percentage of matter in it soluble in pyridine,[1] and also upon the degree of fineness to which it has been ground. The coal-dust used at Frameries contains 20 to 22 per cent. of volatile matter, and is ground to pass a sieve with 1280 meshes to the square cm. (91 to the linear inch). Coal with a higher proportion of volatile matter was found not to grind well. The coal-dust used at Rotherham has, according to Lewes,[2] the following composition :

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[1] Wheeler, *Trans. Chem. Soc.*, 1913, p. 1715.

[2] *Jour. R. Soc. Arts*, 1913, p. 525.

Moisture	2·4 per cent.
Volatile matter	29·6 ,,
Fixed carbon	65·4 ,,
Ash	3·9 ,,

and it ignites at 400°. It is ground to pass a 150-mesh sieve. The amount of moisture in the coal-dust also affects the sensitiveness of the test.

Influence of size of bore.

The influence of the size of the bore of the cannon has been investigated by Hatzfeld at Neunkirchen.[1] Two different cannon were used: the first had a bore of diameter 5·5 cm. and a depth of 57·5 cm., and the other a diameter of 4 cm. and a depth of 70 cm. Tests were carried out with the following three explosives:

(1) Carbonit I		(2) Chrom-ammonite		(3) Wetter-sicheres Gelatine-Dynamit III	
Nitro-glycerine	25	Ammonium nitrate	66	Nitro-glycerine	28·0
Sodium nitrate	30½	Potassium nitrate	14½	Collodion cotton	0·7
Potassium bichromate	5	Chrome ammonia alum	10	Dinitro-toluene	11·0
Wheat flour	39½	Collodion cotton	9	Ammonium nitrate	37·0
		Vaseline	½	Rye flour	4·0
				Sodium chloride	19·3

Of these, chrom-ammonite is now no longer made. Shots were fired into mixtures of fire-damp and air containing 8 to 9 per cent. methane, and also into air mixed with various quantities of coal-dust, of which 2 litres were suspended in the air, whilst the remainder was spread about in the explosion chamber. The charges were fired electrically with a No. 8 detonator. The following Table gives the limit charges:

Diameter of bore-hole	Diameter of cartridge	Explosive mixture	Limit charge of explosive		
			(1)	(2)	(3)
In open	35 mm.	Fire-damp	150	200	50
55 mm.	35 ,,	,,	>700	>700	50
55 ,,	55 ,,	,,	200	550	50
55 ,,	35 ,,	12 litres dust	>700	>600	>700
55 ,,	55 ,,	,,	450	>700	>700

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[1] *S.S.*, 1910, p. 221.

Diameter of bore-hole	Diameter of cartridge	Explosive mixture	Limit charge of explosive		
			(1)	(2)	(3)
55 mm.	35 mm.	7 litres dust	>700	>600	>700
55 ,,	55 ,,	,,	>700	>700	>700
40 ,,	35 ,,	Fire-damp	>700	>650	250
40 ,,	40 ,,	,,	600	>600	300
40 ,,	35 ,,	12 litres dust	>700	>700	>700
40 ,,	40 ,,	,,	>600	>600	>700
40 ,,	35 ,,	7 litres dust	>700	>700	>700
40 ,,	40 ,,	,,	>600	550	>700
40 ,,	35 ,,	2 litres dust	>700	650	>700
40 ,,	40 ,,	,,	>600	500	>700

In practically all cases the explosives were more dangerous when they were concentrated at, and completely filled, the bottom of the bore. Under these conditions the charge would explode in a smaller interval of time, and would consequently give a more violent blow, and the gas mixture at the mouth of the cannon would be heated more strongly adiabatically. In their behaviour towards the various explosive atmospheres the three explosives show characteristic differences. Carbonite on explosion gives a large proportion of reducing gases; when fired from a hole of large diameter at a high density, the explosive is not very safe towards either fire-damp or coal-dust, and this is ascribed to ignition of the combustible products when they have been ejected and mixed with the air. When loaded at lower densities, or fired in a smaller bore, the gases are cooled so much before they reach the mouth that they no longer ignite in the air. Chrom-ammonite, like most ammonium nitrate explosives, contained an excess of oxygen. Consequently there was no danger of the formation of a secondary flame as in the case of carbonite. The explosive showed a high degree of safety under all conditions. The products of explosion of the gelatine dynamite occupy an intermediate position, as the explosive contains nearly enough oxygen for complete oxidation, but not quite. With fire-damp it is the worst explosive of the three, but in the presence of coal-dust it is safe. All three explosives show a lower degree of safety in the larger bore, but this is specially marked in the case of the third. It is true that such large holes are not usually drilled in coal-mines, but when a shot blows out without its proper work, it enlarges the bore somewhat; it is, therefore, desirable to test the explosives in a large hole.

Dimensions of gallery.

It has long been recognized that in a gallery of small sectional area there is greater tendency to cause ignition than in a large one. This question has been investigated at Frameries by Watteyne and Bolle.[1] The explosion chamber of the testing gallery was altered by inserting iron tubes of different diameters, extending from the end, where the cannon is, up to the diaphragm. In this way galleries were obtained with sectional areas of 0·28 and 0·95 square metres, in addition to the ordinary gallery having a sectional area of 2 square metres. Representative explosives of the different types, which have been successful in passing the Frameries tests, were all tried. The following Table summarizes the results obtained: for each explosive the "charge limite" obtained with fire-damp in the 2 square metres gallery is taken as unity, and the "charges limites" under the other conditions are expressed as fractions of this.

Type	Explosive	Tests in fire-damp			Tests in coal-dust		
		0·28 sq. m.	0·95 sq. m.	2 sq. m.	0·28 sq. m.	0·95 sq. m.	2 sq. m.
Safety dynamite .	Dynamite antigrisouteuse V	0·46	0·46	1	≥ 1	≥ 1	≥ 1
Carbonite . .	Kohlen-carbonite .	0·72	0·94	1	0·06	0·28	≥ 1
Gelatine dynamite .	Colinite antigrisouteuse B.	0·56	0·81	1	0·50	≥ 1	≥ 1
Ammonium nitrate.	Fractorite D. .	0·36	0·79	1	0·21	0·43	≥ 1
" " .	Favier 3bis . .	0·33	0·80	1	0·87	≥ 1	≥ 1
Perchlorate . .	Permonite . .	0·06	0·67	1	0·61	≥ 1	≥ 1

The reduction of the "charge limite" with diminution in the diameter of the gallery is only slight with the carbonite when fired into fire-damp, but when coal-dust is present the reduction is very great. The gelatine dynamite contains an equally high percentage of nitro-glycerine, and its products are as combustible as those of the carbonite, but instead of potassium nitrate it contains ammonium nitrate and potassium perchlorate, and this evidently increases the safety. The ammonium nitrate explosives show considerable reduction, as also does Permonite in fire-damp, but not in dust.

It has been proposed by Will[2] to test explosives in a small gallery 3 metres long and 0·21 square metres in section. This might be convenient to manufacturers for making preliminary tests of explosives, but the above figures show that the results could only be received with great caution.

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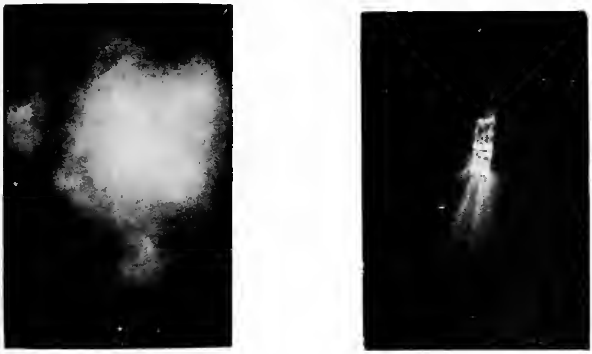
[1] *Annales des Mines de Belgique*, vol. xvi., pp. 289–320; S.S., 1911, pp. 321, 344, and 371.

[2] S.S., 1909, p. 323.

At Liévin numerous experiments have been carried out to ascertain the effect of various factors on the safety of explosives. Various conclusions have been arrived at, which although they leave much yet to be discovered, assist considerably in the comprehension of the matter. These researches were reported on by Taffanel and Dautriche at the 8th Inter. Cong. Appl. Chem., 1912.[1] Complete decomposition, according to the theoretical formula, is nearly always attained in a closed bomb, provided that the density of loading be not too small; and it seems also to be attained in practice in bore-holes that are well tamped; but with most explosives decomposition is very incomplete when they are fired in the steel cannon at the testing stations; when fired in the open air decomposition is still more incomplete. The heat generated was estimated from the pressures registered when the explosion was effected within a very capacious vessel. With safety explosives (Grisoutine, Grisounite, Kohlencarbonite, Sabulite) only about 70 per cent. of the theoretical quantity of heat was evolved when they were fired in a cannon, and only 40 per cent. when unconfined. Dynamite No. 1, on the other hand, detonates almost completely even when unconfined, and so does blasting gelatine, provided that a very powerful detonator be used. These results were confirmed by analyses of the gases: the free oxygen evolved by the safety explosives was considerably less than the theoretical, there were traces of carbon monoxide and sometimes of hydrogen, and considerable quantities of oxides of nitrogen.

Incomplete decomposition



Blasting Gelatine Wetter-Dynamon

FIG. 131. Detonated in the Open. Photographs by Wilkoszewski

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[1] Vol. iv., p. 127.

Flames.

20 g. Blasting Gelatine 100 g. Ammon-Carbonite

FIG. 132. Flame Photographs by Bichel

The liability of an explosive to ignite fire-damp or coal-dust depends, of course, very largely upon the nature of the flame, which it gives when exploded. These flames have been studied by means of photographs for many years past.[1] Bichel, realizing that the time of duration of the flame is of as great importance as its length, photographed through a vertical slit the image of the flame on a sensitive film fixed to a drum which rotated about its vertical axis.[2] He thus obtained an inclined image the height of which gave the length of the flame and the width the duration (*see* Fig. 132). The explosive was fired in a cannon similar to those used at the testing galleries.

The following Table gives some of the results of Bichel's flame measurements:

100 grammes of	Duration secs.	Length mm.	After-flame Ratio
Gunpowder	·077	110	1 : 330
Blasting gelatine	·0097	224	1 : 883
Guhr dynamite	·0083	228	1 : 620
Gelignite	·0012	150	1 : 101
Trinitro-toluene	·0016	108	1 : 1347
Picric acid	·0015	110	1 : 1050
Gun-cotton	·0013	97	1 : 81
Donarite	·00040	69	1 : 15
Ammon-Carbonite	·00028	51	1 : 7·4
Carbonite	·00033	40	1 : 6·5
Kohlen-carbonite	·00031	41	1 : 8·7

The flames from the safety explosives have less duration and length than the others. Other things being equal an explosive with a high velocity of detonation may be expected to give a flame of less duration than a slow one. But a very high velocity of detonation is undesirable in a safety explosive, because it is liable to ignite the explosive gas mixture by the rise of temperature caused

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[1] *See* Guttmann, *J. Soc. Chem. Ind.*, 1899, p. 7; Wilkoszewski, *S.S.*, 1907, p. 141.

[2] *Testing Explosives*, 1905, p. 43; *S.S.*, 1908, p. 408.

by the sudden compression. Biehel, therefore, divided the time of detonation of the charge by the duration of the flame and the figures thus obtained, which he called the "after-flame ratio," he found of use in judging the safety of the explosive.

Fig. 133. Flame from Kieselguhr Dynamite

Will photographs the flames in a somewhat different manner:[1] over a

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[1] *S.S.*, 1909, pp. 323, 343.

circular strip of sensitive film he places a metal disc with numerous small slits in it, and the film and disc are rotated together rapidly behind a small opening, in front of which the cannon is fired. At the same time a photograph of the flame is taken with an ordinary camera (*see* Figs. 133 to 137). These photographs bring out very clearly the secondary flames formed when the products from explosives poor in oxygen, such as gun-cotton, trinitro-toluene or picric acid, become mixed with the air in front of the mouth of the cannon. These secondary flames can be prevented largely or entirely by mixing a few per cent. of an alkali salt with the explosive.

Fig. 134. Flame from Gun-cotton

Effect of alkali salts.

This effect has been confirmed by Dautriche[1] by estimations of the total heat produced when the explosives are fired inside a closed vessel having a capacity of 10 cubic metres, the number of calories being deduced from the pressure generated.

	Heat generated by 100 g.	Heat calculated	
		(*a*)	(*b*)
	cals.	cals.	cals.
Gun-cotton alone	184	96	242
with 0·5 per cent. $NaHCO_3$	146		
1 per cent. ,,	88		
2 per cent. ,,	89		
2 per cent. KNO_3	88		
3 per cent. K_2SO_4	79		
2 per cent. $CaCO_3$	152		
4 per cent. $MgCO_3$	152		
10 per cent. ,,	140		
3 per cent. $Pb(NO_3)_2$	140		
Trinitro-toluene alone	>250	66	354
with 2 per cent. KNO_3	117		
3 per cent. ,,	96		
4 per cent. ,,	82		
5 per cent. ,,	66		
10 per cent. ,,	66		
6 per cent. $Ba(NO_3)_2$	187		
10 per cent. ,,	175		

The figures in column (*a*) are calculated for simple detonation, those in (*b*) for complete oxidation of the products of detonation by the oxygen in the air within the vessel. It will be seen that the salts of the alkalies are much more effective, in preventing the secondary oxidation, than those of the alkaline earths or lead. This is probably due to dissociation of the alkali compounds at the high temperature of the flame, the temperature being thus reduced below the ignition point; the elements recombine at a fairly high temperature so that the heat is available for doing work in blasting.

Also with explosives containing an excess of oxygen the safety is increased by the substitution of a few per cent. of saltpetre for the same amount of ammonium nitrate; the oxidation of the methane by the heated oxygen is, no doubt, similarly prevented by the reduction in the temperature.

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[1] *P. et S.*, vol. xv., 1910, p. 164.

Fig. 135. Flame from Picric Acid

	Charge limite, in grammes	
	Without saltpetre	With saltpetre
Grisounite couche	660	>840
Grisounite roche	240	>670
Grisoutine roche	100	220

With coal-dust the alkaline salts have no marked influence, which shows that the mechanism of the ignition is different.

Effect of density.

The density to which an explosive is compressed has a great influence on the velocity of detonation, and the consequent effect upon the safety of the explosive is in some cases even more marked. Thus Taffanel and Dautriche [1] give the following figures for Grisoutine roche :

Fig. 136. Flame from Picric Acid with 5 per cent. Sodium Bicarbonate

Fig. 137. Flame from Ammon-carbonite

Density	Charge Limite
1·4–1·5	150 g.
1·3–1·4	725 g.

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[1] *Eighth Int. Cong. App. Chem.*, 1912, vol. iv., p. 136.

There was no great difference in the amount of heat evolved, and the "charge limite" of the dense explosive was only raised to 200 g. when it was made up into smaller cartridges. The effect is, therefore, evidently due to the variation in the velocity of detonation. For every explosive there is a critical density, which cannot be exceeded without reducing the "charge limite." This critical density varies according to the nature of the explosive and the amount of moisture in it: sometimes, but not always, it coincides with the limiting density from the point of view of the velocities of detonation. As it is not far removed from the densities to which the cartridges are usually compressed, slight variations in the manufacture of the cartridges, or in the percentage of moisture, may affect greatly the maximum charge that can be fired without causing ignition.

Incorporation. If the ingredients of a safety explosive be not thoroughly incorporated together, the explosion may be greatly affected, and in different cases opposite effects may be produced. Thus in the case of "Grisounite couche" fired in the open, bad incorporation improved the "charge limite," whereas with a Kohlen carbonite fired in a cannon in the presence of coal-dust, the "charge limite" was reduced. The granulation of the explosive also has an influence.

Wrappers. The nature of the material surrounding the cartridge has considerable influence. Taffanel and Dautriche give the results of analyses of gases evolved when "Grisounite roche" is fired from the cannon under various conditions; the means of their results are:

	Oxygen	Combustible gases
	Per cent.	Per cent.
Theoretical decomposition	11·4	0
No wrapper	— 1·1	2·4
No wrapper, a little stemming	1·5	4·0
Asbestos paper wrapper	2·0	1·6
Paraffined paper wrapper	— 1·8	20·0
" " " a little stemming	— 1·5	13·0
Aluminium foil wrapper	— 1·8	2·9
Tinfoil wrapper	— 1·4	2·0
Paraffined paper and 20 g. powdered coal	0	37·5
Tinfoil and 20 g. powdered coal	— 1·1	55·6

The combustible gases comprised carbon monoxide, hydrogen and methane. Considerable quantities of oxides of nitrogen were also formed, including about 3 per cent. of the suboxide N_2O, and some NO which combined with the oxygen of the collecting vessel and caused the deficits of oxygen which were recorded. The figures show that even an explosive containing a large excess of oxygen may give a large proportion of combustible gas. Large secondary flames were obtained in some cases and were recorded photographically. When formed, they greatly reduce the "charge limite," as is shown in the following Table. The "charge limite" in the presence of coal-dust is increased when the amount of paraffin and coal round the cartridge exceeds a certain amount, probably because the temperature of the products is reduced below the ignition point; but it is better to secure this by more certain means, such as the addition of alkali salts.

Nature of wrapper	Explosifs couche				Explosifs roche			
	Grisou-naphthalite		Grisou-dynamite		Grisou-naphthalite		Grisou-dynamite	
	Ordinary	With saltpetre	Ordinary	With saltpetre	Ordinary	With saltpetre	Ordinary	With saltpetre
TESTS WITH FIRE-DAMP								
Ordinary paper	750	1050	1075	—	—	—	< 50	—
Paper slightly paraffined	500	675	—	—	<100	375	—	—
Paper strongly paraffined	175	> 600	150	>400	75	200	< 50	300
TESTS WITH DUST								
No wrapper	—	—	—	—	550	—	650	—
Ordinary paper	>1000	>1000	> 810	—	500	>960	550	>600
Paper slightly paraffined	375	260	—	—	—	—	—	—
Paper strongly paraffined	225	200	360	< 50	< 90	75	< 50	> 50
Asbestos paper	>1400	—	>1290	—	700	—	525	—
Brass	675	—	—	—	—	—	—	—
Iron	550	490	1075	—	220	—	400	—
Tin	> 700	—	> 780	—	430	—	310	—
Aluminium	240	—	—	—	—	—	—	—
Asbestos paper surrounded by coal	175	—	—	—	—	—	—	—
Ordinary paper surrounded by coal	90	180	275	—	—	>800	175	175
Paper slightly paraffined and coal	125	125	—	—	—	—	—	—
Paper very strongly paraffined and coal	> 425	> 900	—	—	—	—	—	—

The above results were obtained by firing cartridges 40 mm. in diameter from a cannon 55 mm. in diameter with no stemming.

Length of the cannon.

The "charge limite" depends not only on the diameter of the bore of the cannon but also on its length. The following results were obtained with a bore 55 mm. in diameter, which was shortened progressively by plugging the bottom with clay. The explosive used was "Grisou-dynamite roche" containing saltpetre :

Length of bore	1·20	1·15	1·00	0·60	metre
Charge limite	275	375	450	525	grammes

This great increase in the "charge limite" cannot be ascribed to the alteration in the position of the charge with respect to the orifice, for if it be left at 0·60 m. from the mouth, with all the clay removed from the cannon, the "charge limite" is again 275 g. Apparently it is the great surface of metal exposed to the products of explosion, which causes the reduction ; and, in fact, it was found by experiment that there was an increase in the amount of heat.

Stemming.

The use of stemming greatly increases the "charge limite." The stemming should be in contact with the charge. The safety can be further increased by placing a quantity of incombustible powder before the mouth of the bore-hole.[1]

Failure to detonate.

It is important that cartridges of explosive should not be broken by careless loading of the bore-hole. For if the explosive become mixed with coal-dust, it may fail to detonate and merely burn, when the detonator is fired. The flame from a charge that is consumed in this way can hardly fail to cause the ignition of fire-damp, if it be present, or of coal-dust, if there be sufficient in the air in the vicinity of the bore-hole.[2] Pulverulent explosives containing excess of oxygen are especially liable to behave in this way. The use of a powerful detonator reduces the danger.

Conclusions.

The manufacturers of explosives have shown great skill in devising mixtures, which shall pass the tests applied in the different testing galleries, and of late years much has been done to investigate the various conditions which cause or prevent ignitions in these galleries, but unfortunately the conditions, under which the charges are fired, are very different from those that prevail in coal-mines. The next step should be to endeavour to devise tests that shall more accurately select explosives that give a reasonable degree of safety. The greatest difference between the conditions in the mine and in the testing gallery is that in the latter the shot is fired in a steel cannon, and in the former in coal, which may be fissured. Another important difference lies in the fact that in the testing gallery the tests are carried out at ordinary atmospheric pressure, but some coal-mines are several thousand feet deep, and consequently the pressure is considerably greater. This high pressure increases the danger of explosion, but it is improbable that the small variations of atmospheric pressure

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[1] *See* Watteyne and Lemaire, *S.S.*, 1912, pp. 21, 43 and 72.

[2] *See* Dautriche, *P. et S.*, vol. xiv., p. 5.

at the surface can have any marked effect on the explosibility of mixtures of air with gas or coal-dust. It has been suggested that when the barometer is falling there is a greater tendency for the fire-damp to escape from the coal. On the other hand, attempts have been made to prove that the majority of mine explosions occur when the barometer is rising.

The strict supervision over the use of explosives in mines has undoubtedly diminished very greatly the loss of life, but the improvements in ventilation and other precautions are also responsible very largely for this diminution.

Classification.

The various classes of safety explosives have been dealt with in previous chapters. They may be divided into six classes, of which the following quantities were used in coal-mines in Great Britain in 1914 :

	Thousands of pounds	Percentage
Black powder mixture (Bobbinite)	1144	13·1
Gelignites with cooling agent	54	0·6
Carbonites	309	3·6
Ammonium nitrate explosives containing nitro-aromatic compounds but no nitro-glycerine	2825	32·4
Ammonium nitrate explosives containing a little nitro-glycerine	2351	27·0
Chlorate and perchlorate explosives	2032	23·3
	8715	100·0

Those in the last class were all potassium perchlorate explosives.

The temperature of explosion may be reduced by having a considerable excess either of oxygen or of oxidizable matter, but in either case the explosive becomes rather dangerous in the mine under certain conditions. For those containing a large proportion of carbonaceous matter give a lot of poisonous carbon monoxide on explosion, and those with an excess of ammonium nitrate or other oxidizer may act on some of the coal in the bore-hole making them more dangerous than under the conditions of the testing gallery. The presence of salts of the alkalies increases the safety, and the temperature of explosion can also be reduced by the addition of inactive cooling agents such as magnesium sulphate or ammonium oxalate. These introduce no fresh sources of danger, but they diminish the power of the explosive.

Hydrated explosives.

American Permissible Explosives sometimes contain hydrated salts, which are added to reduce the temperature, e.g. :

Magnesium sulphate (Epsom salt) .	$MgSO_4.7H_2O$	with	51·2	per cent.	water
Potassium alum	$K_2Al_2(SO_4)_4.24H_2O$	,,	45·6	,,	,,
Aluminium sulphate . . .	$Al_2(SO_4)_3.18H_2O$	,,	48·6	,,	,,
Calcium sulphate (gypsum) . .	$CaSO_4.2H_2O$	,,	20·9	,,	,,

These salts give up some of their water somewhat readily; sodium sulphate commences to effloresce when the moisture in the atmosphere falls to 70 per cent. of saturation.[1] and consequently it will give up part of its moisture to ammonium nitrate. Epsom salt begins to effloresce when the relative humidity falls to 59 per cent.[2]

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[1] P. V. Dupre, *Analyst*, 1905. p. 272.

[2] H. Bolte, *Zeitsch. Physikal. Chem.*, vol. lxxx., 1912. p. 338.

CHAPTER XXX

FIREWORKS

Rocket : War rocket : Life-saving rocket : Display rocket : Sound rocket : Light rocket : Coloured lights : Golden rain : Phosphorus-chlorate mixtures : Railway signals

FIREWORKS are filled with mixtures, which burn energetically and contain in themselves the oxygen necessary for combustion. These mixtures are practically identical with some of those that are used as explosives, and in some circumstances they are liable to explode. Many varieties of fireworks are made to explode in order to produce a report. One of the materials that is very largely used in pyrotechny is mealed powder, to which substances are added to modify its properties or make it burn more slowly.


FIG. 138
Rocket

Rocket.

The rocket consists of a tube, open at one end, into which is rammed black powder mixture. A long conical hole is made in the composition (*see* Fig. 138), and a piece of quickmatch or other igniting device is applied. The composition burns from the surface of the conical hole outwards, and the products of combustion, largely gaseous, escape at a high velocity through the constricted opening, with the result that the rocket is driven forwards. For convenience of loading the composition is sometimes compressed into pellets before being placed in the rocket case. The mixtures used vary considerably in composition :

Saltpetre	57–89 per cent.
Charcoal	16–33 ,,
Sulphur	9–16 ,,

The compositions that burn most quickly are those that do not differ very much from ordinary gunpowder. The incorporation is generally carried out in drums; it is not necessary to mix the ingredients very intimately. The charcoal is often not powdered very finely, in order that a good trail of sparks may be formed as the rocket rises. Practical details concerning the manufacture of rockets and other fireworks are given by G. S. Newth in Thorpe's *Dictionary of Applied Chemistry*, vol. iv., 1913, p. 452.

The ordinary rocket is attached to a stick which projects behind, and serves to maintain the direction as it travels through the air. It is from this that the appliance derives its name, for in Old English and other European languages a distaff was called a "rock." Incendiary rockets were used in warfare as early as the thirteenth century apparently,[1] but seem to have done serious damage only rarely, until they were greatly enlarged and improved about the year 1800, when Colonel Congreve devised his war rocket. This consisted of a strong steel tube which had a cast-iron head and a tailpiece with three conical openings or vents cut away on one side, so that the gas issuing from the body met with resistance on one side only, and so caused the rocket to rotate. The rotation kept the rocket steady during flight and consequently no stick was required. The large war rocket weighed 24 lb. and was about 2 feet long. It was used with great effect during the Napoleonic wars, against Copenhagen, at Walcheren and at the battle of Leipzig, but in consequence of the great improvements in artillery it is never used now. The future may see it revived, like the grenade. A powerful rocket with a charge of high explosive in the head and an impact fuse might prove very effective against an enmy shielded from direct fire, and would be comparatively easy to transport in difficult mountain country. Its worst defect is want of accuracy. Major Unge has attempted to revive it under the name of "aerial torpedo" for the attack of airships, but for this purpose it does not seem to be suitable. The name of "aerial torpedo" has also been given, amongst many others, to the shell thrown by some varieties of trench mortars. Some trials have been made by the Germans with war rockets in the present war, but they are unable to compete with guns, mortars and trench mortars in localities where these can be brought into action.

War rocket.

Life-saving rocket.

The life-saving rocket is used by coastguards and others for throwing life-lines on to wrecked ships. It is a powerful rocket so constructed as to burn for a long time and to put only a moderate strain upon the line. The Boxer life-saving rocket consists practically of two rockets arranged in tandem in the same case, so that when the first has finished burning the second starts.

Displayrocket

The rocket used for pyrotechnic displays has a cardboard case and a chamber in the forward end, separated by a plug of clay or other material through which passes a piece of quick-match. The chamber contains gunpowder and a number of stars, composed of white or coloured light composition and primed with mealed powder. When the rocket has reached its maximum height and all the rocket composition has burnt away, ignition is conveyed by the quick-match to the powder, which explodes and bursts the walls of the chamber.

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[1] *See* Hime, *Gunpowder and Ammunition*, p. 172.

The stars then fall down burning brightly. The signal rockets used for military purposes are constructed in the same way.

Sound rocket. Sound rockets, which are also used for signals, have a small charge of tonite or other high explosive, which is fired by means of a detonator as soon as the rocket composition has burnt away.

Light rocket. Light rockets are used to light up the landscape and reveal the position of the enemy at night. Each rocket usually contains a single star composed of light composition somewhat similar to that used for photography. This consists of powdered aluminium or magnesium-aluminium alloy mixed with oxidizing materials such as barium nitrate and potassium chlorate. The tendency is to substitute aluminium powder partly or wholly for the magnesium, as it gives quite as good a light and is cheaper. As stated in the last chapter the presence of potassium nitrate in a mixture diminishes the temperature, hence it is better to use barium nitrate. These stars are sometimes provided with parachutes.

Coloured lights. Coloured lights are used not only for the stars of rockets but also for Bengal lights and very many other sorts of fireworks. In books devoted to pyrotechny many different formulae may be found, but it may be stated generally that for

green lights	barium compounds
yellow lights	sodium compounds
blue lights	copper or lead compounds
red lights	strontium compounds

are used. Fire-workers like to use the chlorates of these elements together with sulphur or a sulphide, as such mixtures burn with great brilliancy. But such compositions are decidedly dangerous: not only are they very sensitive to blows and friction, but they are even liable to ignite spontaneously. The sulphur is oxidized by the chlorate to sulphuric acid, which then accelerates the reaction until it becomes so rapid that the mass ignites. Mixtures containing sulphur are considerably worse than those with sulphides, and after a number of fatal accidents had occurred the use of the sulphur-chlorate mixtures was definitely forbidden by Order in Council No. 15 of April 30, 1894. A similar order has also been issued in India, partly because these mixtures were used by Indian anarchists, but in consequence of the difficulty of enforcing such a regulation in a country like India, they are still made by village firework makers, and lead to many fatal accidents. Reports of the following accidents were received, but it is possible that others occurred, though not reported:

Year	Accidents	Killed	Injured
1909	15	6	28
1910	16	23	53
1911	8	2	15
1912	8	2	12
1913	8	5	13
1914	2	1	9
1915	0	0	0

Mixtures of chlorates with the sulphides of arsenic, antimony and copper are also dangerous.[1] Shellac, which is much used for binding the composition together, increases the sensitiveness.[2] Mixtures of chlorate, metallic aluminium and shellac are specially dangerous and may ignite spontaneously if kept at a temperature of 100° F. (38° C.). In many cases the chlorates may be replaced with advantage by the more stable perchlorates. In most countries mixtures of chlorate and sulphur are still allowed. Even in England it is permitted to prime chlorate stars with mealed powder, which is usually applied moist, and a small quantity of chlorate-sulphur mixture is thus formed: several accidents have been ascribed to this cause. Chlorate mixtures are somewhat difficult to ignite, hence the necessity of having a priming of some mixture, such as mealed powder, more easy to ignite. But a composition containing no sulphur would be safer. Stars made of chlorate mixtures are rammed into "pill boxes," and are provided with a little priming, as already stated. Those made of nitrate mixtures are generally "naked," as they burn more quietly and require no priming. Sodium chlorate compositions are more dangerous than those containing the potassium salt.

The following test for spontaneous ignition is applied by the U.S. Bureau of Explosives:[3] A sufficient quantity is taken to furnish 50 grammes of the explosive composition. The covering is perforated or slit to facilitate the absorption of moisture, and 10 c.c. of water is added so as to be completely absorbed by the 50 grammes of composition, which is then wrapped in a number of folds of towelling or cheese cloth. It is then placed in a glass jar or bottle whose interior dimensions approximate to those of the bundle, and whose mouth can be securely closed by a screw top with a suitable gasket. The jar or bottle is then placed in a boiling-water oven for 48 hours. The composition should not ignite spontaneously.

The following are some examples of coloured fire mixtures:

Green		Yellow		Red	
Barium chlorate	66	Sodium nitrate	70	Potassium chlorate	78
Milk sugar	33	Sulphur	20	Strontium carbonate	15
Shellac	1	Antimony sulphide	7	Shellac	7
		Lampblack	3		

Blue		White	
Potassium chlorate	45	Saltpetre	66
Shellac	5	Sulphur	16
Charcoal	5	Antimony sulphide	16
Basic copper carbonate	10	Gelatine	2
Calomel	35		

The compositions have to be varied somewhat according to the rapidity with

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[1] *See A.R.*, 1905, p. 219; *S.R.*, No. 195, p. 6.

[2] *See S.R.*, No. 148.

[3] *Fourth Annual Report of Bureau of Explosives*, 1911.

which they are required to burn, and the conditions of use. For blue light, alum is sometimes used instead of, or in addition to, copper compounds. To white lights a little lead oxide or nitrate is added in some cases to neutralize the yellow effect due to traces of sodium salts. Calomel (mercurous chloride) is often added, especially to blue and red lights, to increase the luminosity and decrease the rate of burning.

Golden rain.

Golden rain is made by mixing powder, such as is used for rockets, with crushed iron or steel turnings or borings. These materials are also often added to the rocket mixtures in order to produce a more brilliant trail. If the borings are uncrushed, comparatively few sparks are formed, but they are finer individually and give a good scintillating effect. Magnesium or aluminium powder gives white sparks; copper, greenish ones; zinc, bluish white; and iron, red.

Phosphorus-chlorate mixtures.

Mixtures of chlorates with phosphorus are considerably more dangerous than those with sulphur, and their use in fireworks was restricted by Order in Council No. 19 of January 12, 1905, which directs that "no firework which contains an admixture of phosphorus (whether or not in the amorphous form) with chlorate of potassium or other chlorate, shall be manufactured, imported, kept, conveyed, or sold, unless such firework shall have been specially licensed by the Secretary of State for manufacture or importation, and unless it is named and defined in a List of Authorized Explosives signed by a Government Inspector and in force for the time being." Restrictions are imposed in order to ensure that the articles manufactured shall not be capable of exploding in bulk. Thus an Alarm Cork is not allowed to contain more than 0·4 grain (0·026 g.) of mixture, of which not more than 15 per cent. may be phosphorus (amorphous). Amorces or caps for toy pistols, snaps for bon-bon crackers and similar articles, must not contain more than 70 grains of composition per 1000, of which not more than 10 grains may be phosphorus. Fulminate of silver is also used, but in this case the quantity must not exceed 15 grains (1 g.) per 1000. In Germany only 0·5 g. per 1000 is permitted; on the other hand, the charges of chlorate and phosphorus in explosive corks are comparatively large, and a number of fatal accidents have occurred through their exploding in bulk in Germany and in the United States, whither they were allowed to be exported until a few years ago. In England the quantity of fulminate of silver allowed in the work-rooms is usually limited to 1 grain per person.

Railway signals.

The railway fog signals used in England consist of flat tins filled with gunpowder and containing a number of percussion caps. Soldered to the top is a strip of lead, by means of which it is attached to the rail. When a wheel of the train passes over it it fires the percussion caps, which explode the gunpowder. The signals must be so constructed that if one explodes it will not fire others in contact with it.

In America "railroad fusees" are used, which are practically coloured lights, intended to burn for about 10 minutes. The top is provided with a little match composition which can be ignited by rubbing on a prepared surface. The most usual colour is red, and formerly they generally contained strontium nitrate, potassium chlorate, sulphur, resin, charcoal, petroleum grease and sawdust. The mixture of chlorate and sulphur made them liable to spontaneous ignition and unduly sensitive. They have now been rendered safe by the elimination of the sulphur or the substitution of potassium perchlorate for chlorate. The perchlorate must not contain more than 0·5 per cent. chlorate.[1]

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[1] *See Bureau of Explosives Report*, No. 3, p. 35, and No. 5, p. 50.

PART XI

STABILITY, ETC.

CHAPTER XXXVII

BUILDINGS, ETC.

Construction : English distances : German distances : Austrian : American : Effects of explosions : Concrete buildings : Tunnels : Gutters : Mounds : Lighting : Lightning conductors : Frictional electricity : Interiors : Barriers, etc. : Clothing : Small magazines : Thaw-houses : Tropical magazines : Conveyance of explosives : Ship's magazines : Naval catastrophes : Gas explosions : Spontaneous ignition : Repair of danger buildings : Warnings

Construction.

In the early days of gunpowder-making special factories were not erected, but the explosive was compounded in ordinary buildings which were frequently situated in thickly populated towns, and sometimes blew up with disastrous results. As the scale of manufacture increased, it was found necessary to build powder-works in isolated places, and a special type of building was gradually evolved. It was found advisable to have the roof and at least one wall of light construction, as the force of the explosion of gunpowder is greatly reduced when the resistance offered is small ; the weight of the debris projected is also diminished. For buildings in which high explosives undergo manufacturing operations it is generally considered that all the walls, as well as the roof, should be of light construction. The general principles governing the construction of danger buildings were stated by H.M. Inspectors of Explosives in *A.R.*, 1909, p. 5 :

"(1) In working buildings, from which all the explosive is removed on completion of the day's work, the more flimsy the construction the better. In view of the distances to which heavy masses of debris have been thrown by explosions, the soundness of the principle is obvious. The actual material recommended is match-boarding, corrugated iron, or sheets of light fire-resisting material. For roofing, slates and tiles are dangerous, and tarred felt carries fire, so that only corrugated iron and fireproof sheets remain, and there are objections to these ; in fact a good roofing material for working buildings containing explosives is much wanted.

"(2) In magazines, on the other hand, where explosive is present at all times, but where as a rule it is contained in securely closed packages, the chief danger to be anticipated is from unauthorized entry, and a substantial construction of brick, masonry or concrete is called for. An exception to this is made in the case of a factory, where a watchman is always present at night, on Sundays, and during holidays, in which case a reasonably stout corrugated iron is allowed.

"The lining of a danger building need not necessarily be of wood. 'Neat' cement, *i.e.* cement free from sand, or any other material satisfying the conditions of General Rule No. 2,[1] may be used. In fact, in very dusty buildings a lining which can be effectively washed down by means of a hose has many advantages.

"The floor should be of soft material, such as wood or asphalt, free from grit: care being taken to fill up all interstices and crevices in which explosive dust may accumulate. Doors should open outwards and, while any one is in the building, should only be secured in such a manner as to be opened easily by a push. There should be plenty of them, and so far as practicable they should face towards the path by which a work-person would naturally endeavour to escape."

For roofing danger buildings rubberoid has been adopted in some cases. Although it is distinctly inflammable, it is readily extinguished when projected through the air.[2] The objection to a very light roof is that heavy debris, possibly alight, may be projected through it from the explosion of another building. Nevertheless a light construction has decided advantages. The dividing walls between different compartments of the same building, if of brick or stone, should extend well above the roof.[3]

The use of exposed iron should be avoided in the floors and anywhere where it may come in contact with sensitive explosives. Lead, iron and lime or whitening must not be used where picric acid or picrates are dealt with. The use of tin in the construction or repair of apparatus or utensils to be used in the manufacture of gunpowder mixtures or fireworks was formerly forbidden in Germany, because the basic tin nitrate, that is liable to be formed, is sensitive to blows, friction and heat. The matter was, however, re-investigated by Will, who found that under ordinary conditions very little tin nitrate is formed, and that the danger was greatly exaggerated.[4]

Picric acid buildings are best constructed of wood. On the other hand wood should be avoided in building nitric acid factories and stores for nitrates, as wood impregnated with nitrate is very inflammable and burns fiercely.[5]

Cordite stoves and other buildings in which nitro-glycerine vapour is present should not have separate linings behind which nitro-glycerine may accumulate. It is better to provide them with a facing of neat cement. The same applies to the floors of magazines for dynamite, and other explosives that are liable to exude nitro-glycerine.[6]

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[1] *See* Guide to Explosives Act, p. 141.

[2] *See A.R.*, 1910, p. 5.

[3] *See S.S.*, 1910, p. 33.

[4] *Chemische Industrie*, 1912: *S.S.*, 1912, p. 289.

[5] *See S.S.*, 1911, p. 418.

[6] *See S.R.*, No. 210.

English distances.

A most important measure of safety is the requirement that magazines and other danger buildings are not allowed within certain distances of other structures or places where people are liable to be. H.M. Inspectors of Explosives have published a Table of these distances, an extract from which is given on the following pages. The distances are reduced to half in any case where the magazine or danger building is effectively screened, either by the natural features of the ground, or by good and substantial artificial mounds of such a height that a line drawn from any part of the magazine or danger building will pass through the intervening ground or mound. When a natural hill intervenes, the Inspector may permit reduction to one-quarter, but in no case is the distance from His Majesty's palaces to be less than two miles. The reduction on account of mounds is only allowed in the case of quantities exceeding 1000 lb., but for mounded buildings containing 100 lb. and under, situated within the same factory, a special Table is maintained by the Inspectors, and may be seen on application. As cordite of large size has never been known to explode even when very large quantities have been burnt, it is considered to constitute a fire risk only if of size 16 or upwards and in quantities not exceeding 1000 lb.[1]

German distances.

In 1908 the German Trade Guild for Chemical Industry adopted a scale of distances for the buildings in factories for nitro-glycerine explosives: for the buildings comprising a system, the distances are generally:

Permissible quantity of explosive .	kg.	600	1200	2000
Distances	metres	25	40	50

These distances are measured from the centre of one building to that of the other, whereas the English distances are measured from the exterior walls of the buildings. The buildings in Germany must be surrounded by earth mounds 1 metre higher than the ridges of the roofs. The distances are less than those in line (2) of the English Table, even after the latter have been halved on account of the mounding of the buildings, but a direct comparison cannot be made because the method of measuring the distances is different. In washing-houses for nitro-glycerine, double the above quantities are allowed for the same distances. In a magazine for nitro-glycerine 4000 kg. are allowed, and it must be at least 30 metres from any other building.

The different systems within a factory must be distant at least 80 metres from one another or from the cartridge huts, the distance being measured from the outside walls of the buildings. From the machinery buildings, laboratory and other non-danger buildings directly connected with it, the system must be distant 100 metres; and from the offices, gun-cotton works, engineers' shops and other non-danger buildings not connected with it, the distance must be 250 metres. The following Table gives the distances for the other danger buildings of a factory for nitro-glycerine explosives:

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[1] *A.R.*, 1912, p. 27.

DISTANCES FOR MAGAZINES AND

The figures in brackets are the distances to be observed when gunpowder

When such distances are assigned, 2 lb. of manufactured fireworks or ½ lb. of

Amount of explosives to be allowed in the magazine or danger building	lbs.	300	500	1000	2000
(1) Room in connexion with the magazine, for filling cartridges for small-arms (in which 5 lb. of explosive is allowed unloaded: section 46 of Act)	yards	(25)	50 (35)	50 (35)	50
(2) Mineral or private railway: highway or other open place of resort; canal, reservoir, etc.: workshop in connexion with magazine for preparing charges for blasting (in which 100 lb. gunpowder or 50 lb. of other explosive may be present: section 47); buildings and magazines inside the same factory: two or more magazines belonging to the same occupier, or by mutual consent of the respective occupiers	..	(25)	50 (35)	75 (50)	100 (75)
(3) Other magazine or store for explosives, or room or workshop in connexion therewith: furnace, kiln, or fire for the use of any boiler, engine, or machine, or for any manufacturing purpose	..	(50)	100 (65)	150 (100)	200 (150)
(4) Public railway	..	(50)	100 (65)	150 (100)	200 (150)
(5) Dwelling-house *with* the consent in writing of the occupier	..	(25)	50 (35)	75 (50)	100 (75)
(6) Dwelling-house *without* such consent: factory not belonging to Government: Government factory or magazine with consent: theatre or other building, where people are accustomed to assemble	..	(50)	100 (65)	150 (100)	200 (150)
(7) Government factory or magazine without consent	..	(440)	880 (585)	1320 (880)	1760 (1320)
(8) Palace or house of residence of His Majesty, his heirs and successors	miles	2	2	2	2

THER DANGER BUILDINGS

or cordite in cords not contained in metal cases only are stored.

any other explosive may be reckoned as equivalent to 1 lb. of gunpowder.

3000	4000	5000	6000	7000	8000	9000	10,000	10,000 to 100,000 lb.
51	52	52	53	53	54	54	55	50 + ·0005 e. where e is the quantity of explosive
101 (90)	102	104	105	106	108	109	110	100 + ·001 e.
200 (175)	200	200	200	200	200	200	200	150 + ·005 e. up to 20,000 lb. 100 + ·0075 e. 20,000 to 100,000 lb.
210 (175)	215 (200)	225 (210)	235 (220)	240 (230)	250 (245)	255	265	200 + ·0065 e.
110 (90)	120 (100)	130 (110)	140 (125)	145 (140)	155 (150)	165 (160)	175	100 + ·0075 e.
240 (175)	280 (200)	320 (255)	365 (310)	405 (360)	445 (415)	485 (470)	525	200 + ·033 e.
1780 (1540)	1805 (1760)	1825 (1790)	1850 (1820)	1870 (1850)	1890 (1880)	1910 (1905)	1930	1760(1 + ·0001 e.)
2⅛	2¼	2¼	2⅜	2½	2½	2⅝	2¾	2 + ·00008 e.

	Distances Centre to centre		Limit for explosives	Limit for workers
	metres		kg.	No.
Cartridge huts for high per cent. explosives	12		50	2
	15		75	
Cartridge huts for low per cent. explosives	15		200	4
Packing-houses	30		No accumulation	6
	From one another	From the packing-houses		
Magazines for explosives	15	40	5,000	—
	40	150	30,000	—
Drying house for collodion cotton	45			2

High per cent. explosives are those that contain 25 per cent. nitro-glycerine or more, low per cent. ones contain not more than 5 per cent.

Austrian distances.

In Austria-Hungary distances from magazines and laboratories have been laid down in the regulations for the care of material.[1] The objects, from which distances are specified, are divided into two classes; class 1 comprises buildings in which there is no fire, and roads and paths that are little used, and factory buildings not directly devoted to manufacture; class 2 comprises all buildings, railways, roads and paths, where the results of an explosion might be disastrous.

	Capacity	Class 1	Class 2
		Distance in metres	
Powder or explosive magazine	Up to 100 kg.	100	100
.. .. ..	100–1000	200	300
.. .. ..	1000–3000	300	500
.. .. ..	over 3000	400	750
Shell magazine	No limit	200	400
Small-arm ammunition magazine	No limit	50	50
Laboratories in which explosives are dealt with	—	200	300

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[1] *See S.S.*, 1910, p. 177.

These distances may be diminished if effectual protection is afforded by mounds, trees or natural features of the ground. The rules do not apply to military magazines. The distances are greater than the corresponding ones in the English Table.

American distances.

In 1910 a committee of American manufacturers, with the assistance of the Chief Inspector of the Bureau of Explosives, made a study of all the recorded explosions throughout the world, and from the results drew up a Table, which has been adopted officially in the United States for explosives magazines.

Pounds of explosives	Inhabited buildings (feet)	Public railway (feet)	Pounds of explosives	Inhabited buildings (feet)	Public railway (feet)
50	120	70	10,000	890	535
100	180	110	20,000	1,055	635
200	260	155	30,000	1,205	725
300	320	190	40,000	1,340	805
400	360	215	50,000	1,460	875
500	400	240	60,000	1,565	940
600	430	260	70,000	1,655	995
700	460	275	80,000	1,730	1,040
800	490	295	90,000	1,790	1,075
900	510	305	100,000	1,835	1,100
1,000	530	320	200,000	2,095	1,255
1,500	600	360	300,000	2,335	1,400
2,000	650	390	400,000	2,555	1,535
3,000	710	425	500,000	2,755	1,655
4,000	750	450	600,000	2,935	1,760
5,000	780	470	700,000	3,095	1,855
6,000	805	485	800,000	3,235	1,940
7,000	830	500	900,000	3,355	2,015
8,000	850	510	1,000,000	3,455	2,075
9,000	870	520			

These distances are for magazines that are "barricaded," that is, screened from other buildings or railways by either natural or artificial barriers. Where such barriers do not exist, the distances shown should be at least doubled. A comparison of the English with the American Table of distances shows that the latter requires greater distances for the smaller quantities of explosives, whilst the English Table requires greater distances for the larger quantities, but does not contemplate that more than 100,000 lb. will be placed in one magazine.

Effects of explosions.

Experiments have been carried out at various times and places to ascertain the distances at which explosions will produce a specific effect according to the quantity of explosive. Such experiments have been performed at Kummersdorf in Germany, and at Arendonck and Bewerloo in Belgium, and in 1902 to 1904 an extensive series was carried out in France.[1] In the French experiments different quantities of various explosives were exploded in the open, and at various distances a number of little screens were erected, so arranged that the same degree of force would cause each of them to fall back. It was thus possible to ascertain the distances at which the same effects were produced. The most simple theory would lead one to expect that the distance would be proportional to the square root of the weight of the charge. These experiments, which were carried out with quantities of 0·1 to 100 kg. of melinite, 150 kg. of cheddite, and 300 kg. of gunpowder, were in agreement with this theory. They were confirmed by trials in which small huts with glass windows were exposed to the effects of the explosions at various distances. This rule is expressed by the equation $d = k.\sqrt{c}$, where d is the distance, and c the weight of explosive, and k a constant depending on the nature of the explosive and the sort of damage considered. For high explosives causing the breaking of window panes and slightly injuring the frames and wooden walls $k = 10$ about, the distances being measured in metres and the charges in kilogrammes. Up to 30,000 lb. this equation gives greater distances than those in line (6) of the English Table, but above that quantity it gives smaller distances. With gunpowder double the quantities are required to produce the same effects, or $k = 7$. This is in agreement with the English Table up to quantities of about 2000 lb.

Lheure also determined the velocity with which the impulse is transmitted through the air. Near the seat of the explosion the velocity is much greater than the normal velocity of sound, but it falls off rapidly and, at about the distance at which window-panes are no longer broken, the velocity is the same as that of sound. The more brisant the explosive the greater is the initial velocity of the impulse. Increase of the quantity of explosive does not seem to increase the initial velocity, but it causes the rate of diminution to be less.

The figures in the American Table do not agree very well with an equation of the above form. For small quantities the distances are more nearly proportional to the cube root of the weight of explosive, and for very large quantities the variation of the distance is more nearly proportional to the increase of the weight. It is somewhat doubtful whether the equation really represents the results obtained under practical conditions. The records of explosions do not indicate that any distinction should be drawn between gunpowder and high explosives, when quantities of several tons are concerned.

When black powder explodes in a magazine, the structure offers so much less resistance than the ground, that nearly all the energy of the powder is

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[1] *See* Lheure, *P. et S.*, vol. xiii., p. 161 ; *S.S.*, 1907, pp. 228, 249, 308, 427, and 446.

expended in an upward or sideward direction, even though the magazine be of strong construction. When a high explosive detonates, a larger proportion of the energy is expended in a downward direction, because the time occupied by the explosion is much shorter, and the air offers considerable resistance to the almost instantaneous evolution of gas. Consequently, when a large quantity of nitro-glycerine or other high explosive goes off, a severe wave of concussion is transmitted through the earth at the same time as waves are sent through the air. Guttmann has laid great stress on the earth-waves,[1] but except in the case of an underground building the energy expended on the air must be greater than that expended on the ground, and consequently most of the damage done by an explosion is due to the air-wave. That this is so is confirmed by the fact that the provision of a mound round a danger building reduces the area of destruction to about half, for the mound can only give protection against air-waves and flying missiles. In the case of explosions in nitro-glycerine factories, the earth-wave is often much reduced by the fact that the tanks containing the explosive do not rest upon the ground, but are supported some distance from it on a staging. Guttmann has suggested that danger buildings should be built over pits in order to reduce the concussion of the earth.

FIG. 139. Building wrecked by Explosion 30 yards away. Ardeer, February 27, 1897

It is noticed that in buildings near the seat of an explosion the windows and doors are blown in, but at a greater distances they are sucked out, so that the broken glass, for instance, all lies outside the building. This difference is shown by the two photographs (Figs. 139, 140) taken from Guttmann's paper. The first shows the crushing in of a nitro-glycerine separating-house distant 30 yards from the site of the explosion of 1800 lb. of nitro-glycerine, and the other the sucking out of the walls of a building situated 145 yards from a glazing house in which 7000 lb. of gunpowder exploded.

The gases formed in the explosion are only projected to comparatively small distances. In the Faversham explosion of February 21, 1879, where

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[1] *J. Soc. Chem. Ind.*, 1908, p. 669; *S.S.*, 1908, p. 266

the conditions were peculiarly favourable to their projection laterally, the scorching effect did not extend beyond 50 yards,[1] whereas serious structural damage was done at 283 yards, and windows were broken at a distance of a mile. A wave of compression is set up, which travels through the air in all directions, and is immediately followed by a wave of rarefaction, or rather there is a complete wave which consists, like an ordinary sound-wave, of compression followed by rarefaction, and this is followed by other similar waves each more feeble than its predecessor. As the waves travel away from the place of origin, the compression part of the wave becomes shorter and the rarefaction portion longer, so that beyond a certain distance the effects of the latter exceed those of the former.

FIG. 140. Building wrecked by Explosion 145 yards away. Faversham, February 21, 1879

Concrete buildings.

The direction in which the air-waves can do least damage is the upward one. Hence the desirability of having a light roof and surrounding the danger building with substantial mounds. But unfortunately the light roof introduces other dangers, for if one of the other buildings in the factory be blown up, a piece of machinery, or of the building, may be projected right through the roof and cause the explosive within to go off too. There have been several instances in which the extent of a catastrophe has been greatly increased in this way. It is partly on this account that magazines are usually built with substantial walls and roofs. In the experiments carried out at Kummersdorf in 1897 and 1899 quantities of 1500 and 500 kg. of gelatine dynamite were exploded in small magazines constructed specially of fine gravel concrete, and it was found that this material was entirely broken up, so that no large masses were projected about. On the other hand, in some experiments carried out in France, in which quantities of 25 kg. of Dynamite No. 2 were exploded within small magazines made of concrete, armoured and unarmoured, it was found that considerable pieces were projected 50 metres, and smaller fragments 75 metres.[2] The difference from the results obtained in Germany may have

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[1] *S.R.*, No. 22, p. 7.

[2] *P. et S.*, vol. xv., 1910, p. 177.

been due to some difference in the composition of the concrete. Safety is further increased by covering the magazine with a layer of earth, which will arrest any considerable pieces of the fabric. For new magazines erected in Germany for the storage of high explosives this method of construction is now generally adopted (*see* Fig. 141). They are made of gravel concrete without any admixture of sand. The walls are at least 60 cm. (2 feet) thick, the roofs are vaulted and covered with a layer of earth at least a metre thick. There are double doors, of which the outer is of oak at least 5 cm. (2 inches) thick.

In an explosion of 700 or 800 kg. of Gelignite, which occurred in 1907 at the Carbonite Works at Schlebusch, a magazine of this sort, distant only 60 metres from the explosion, was not injured in any way.

Guttmann proposed to construct all the danger buildings of factories for high explosives of armoured concrete with walls 20 cm. (8 inches) thick, containing iron tie-rods 6 to 12 mm. ($\frac{1}{4}$ to $\frac{1}{2}$ inch) in diameter.[1] The roof also was to be of concrete, but double, with a layer of sand 36 cm. (1 foot 5 inches) between, in order to arrest any missile which penetrated the outer layer of concrete. At the Seventh International Congress of Applied Chemistry held in London in 1909 Bichel objected to this method of construction on the ground that it is too heavy and too unstable.[2] Subsequently Guttmann adopted another method for the construction of the roofs of these danger buildings: [3] he made them of light but strong wooden beams protected above and below with expanded metal or wire netting, the whole being covered with corrugated iron to keep out the rain. Such a roof offers great resistance to objects falling upon it.

Bichel also has constructed danger buildings of armoured concrete, but he covers them entirely with earth except on one side, which consists mostly of glass.[4] The general design is very similar to that of the magazine shown in Fig. 141, but inside the vaulted roof made of fine gravel concrete, there is another roof 8 cm. thick made of armoured concrete, with an air space of 4 cm. between the two. In front of the glass side of the building there is a high mound, a short distance away, through which access is provided to the building by means of a short straight tunnel. The mouth of this tunnel is protected by means of another mound. It has been found that a long tunnel leads to the formation of a very long flash in the case of an explosion, and making the tunnel with a bend in it does not add to the safety, but is liable to cause the tunnel to collapse. **Tunnels.**

Danger buildings in which large quantities of explosive are dealt with

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[1] *J. Soc. Chem. Ind.*, 1908, p. 669; *S.S.*, 1908, p. 266.

[2] *See* Report of Section III B, p. 49.

[3] *J. Soc. Chem. Ind.*, 1910, p. 930; *S.S.*, 1910, p. 265; Eng. Pat., 4094 of 1909.

[4] *Loc. cit.*; *also S.S.*, 1910, p. 182; *Chemische Industrie*, 1912, p. 139.

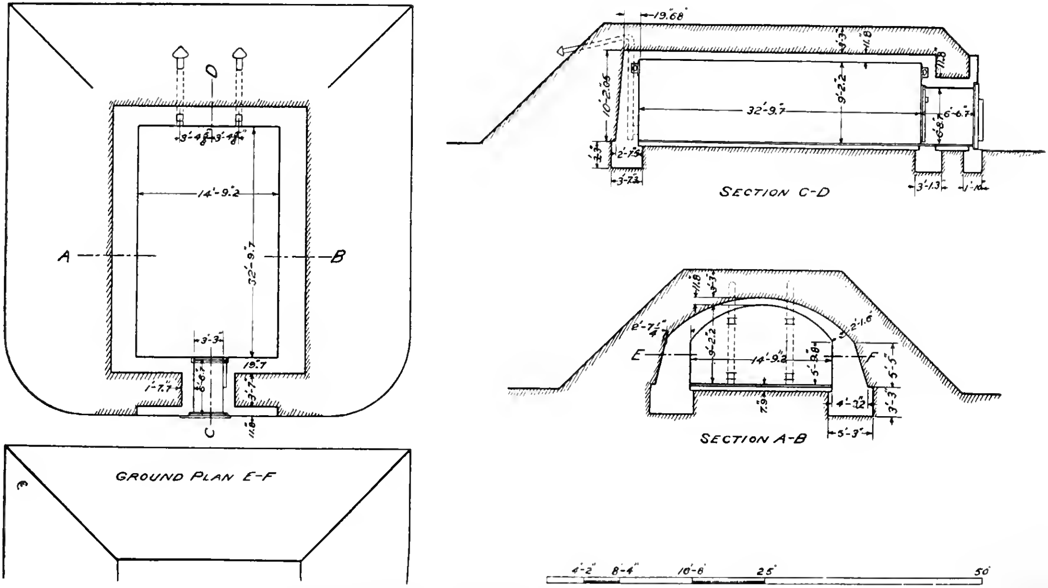

Fig. 141. Magazine of Carbonite Explosives Co., Schlebusch
(From *Bureau of Mines Technical Paper*, No. 18)

should never be connected directly with one another by tunnels or passages. The gutters for the conveyance of nitro-glycerine from one building to the next are also a source of danger. They should be connected to the plant at either end only by rubber tubes, which should be disconnected except when nitro-glycerine is actually being transferred. The gutters should be covered over by thin canvas only, to avoid the communication of explosion from one building to the other by means of long flames. Perhaps it would be better not to have them covered in, but merely protected by means of a roof raised some distance above the edges.

Gutters.

Mounds.

Mounds or traverses are erected round danger buildings to prevent the explosive wave travelling horizontally to other danger buildings near. They have been made of various materials. Earth alone is effective and safe, but occupies a lot of ground. Earth confined between sheets of corrugated iron is also good. Concrete containing only a small proportion of cement may also be used, as it will break into small fragments in the case of an explosion. Mounds of sand with brick revetments have been used in South Africa, and have been found satisfactory in the case of high explosives, as the bricks are pulverized by the detonation. But with a lower explosive, such as gunpowder, whole bricks would probably be projected with possibly disastrous results.[1] Mud (adobe) or bricks of dried clay, unburnt, would probably be safe. Where the locality permits one side of building may be unprotected by mounds so as to allow the explosive wave to travel in that direction. This "blow-out" system has proved effective in some instances.[2]

Lighting.

For the artificial lighting of buildings in explosives factories electricity is used almost universally. Electric incandescent lamps are used preferably mounted in the walls in recesses separated from the interior of the building by a thick pane of glass. All the wires and connexions are outside the house. If the lamp must be placed in the middle of the room, it should be protected by an outer bulb of glass so thick that a blow that will break it will also break the filament of the lamp. In the case of magazines electric current is not always available; lamps containing candles or burning rape oil should then be used, and they should be mounted in the walls in recesses that can only be opened from outside the building. For portable lights electric hand-lamps or electric torches are best, but for magazines where the explosives are in packages rape oil or candle lamps are used sometimes.

Sky-lights should be glazed with glass having wire insertion to prevent the danger of particles falling inside. This precaution is not so necessary in the case of windows in the walls. Except for windows facing north the glass should be corrugated or dulled with whitening to prevent the direct rays of the sun shining on explosives in the building.

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[1] *See A.R.*, 1904, p. 52.

[2] *See S.S.*, 1912, p. 170.

Lightning conductors.

Some danger buildings and all magazines, except those which contain only very small quantities of explosive, must be provided with lightning conductors. In spite of all that has been written on the subject most architects, engineers and builders seem to think that effective protection against lightning is provided by running a copper tape or rope up a building and connecting it with a metal point fixed on to the ridge of the roof. The lightning is expected to follow obediently all the turns and twists in the conductor, and never to spring across and take short cuts, which, however, is just what it always does. The vast majority of the lightning conductors are calculated rather to conduct the lightning into the building than away from it. Fortunately, severe thunderstorms are rare in England and many other countries, and so the futility of these appliances is not rendered evident. In South Africa and in some parts of Germany the same immunity is not enjoyed, and a number of catastrophes have led to much careful thought being given to the subject of protection from lightning.

Nitro-glycerine factories are specially liable to be struck. The top of the nitrating house is necessarily raised a considerable height above the lower portions of the system, and the large masses of metal within the house add to the danger. Moreover, a comparatively small spark, which would do no serious damage in an ordinary building, will suffice to explode the nitro-glycerine, so that a building may be blown up without being struck directly. If the lightning strike the ground near by, it may set up such powerful induced currents that the nitro-glycerine will be exploded. In 1895 Major Cardew drew up an elaborate scheme for the protection of nitro-glycerine factories in South Africa.[1] On each side and at the ends of each line of buildings to be protected, hollow iron pillars about 40 feet high were to be erected, their lower ends being sunk about 10 feet in the ground. To counteract the extreme dryness of the soil perforated water-pipes were to be led up into each of the pillars so that, when deemed advisable, the pillars themselves and the earth at the base might be thoroughly drenched to reduce the resistance of the earth. Circles of points were to be fixed to the pillars at intervals of 10 feet or so. The buildings themselves were, if practicable, to be of galvanized iron sheets, but if this could not be done, a screen of iron wire netting was recommended. It was suggested that this netting should be supported by wire ropes attached to short iron poles on the mounds, these short poles being provided with points, and being connected by means of stout wire rope to the above-mentioned high pillars.

As regards the masses of metal in the buildings and the pipes leading into them, it was pointed out that the danger is twofold: either they may be charged inductively, with the consequence that sparks will pass when the flash occurs, or they may act as alternative paths for the whole or part of the

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[1] *See S.R.*, No. 179.

flash. The first of these contingencies may best be provided against by thoroughly "earthing" each separate piece of metal, and the second by connecting electrically all masses of metal to one another and to the protecting system, or by separating them by so large a gap as to eliminate the risk of communication. It was pointed out that it is not even safe to have sharp portions of two metal masses very close together, although the masses themselves may be connected by a metallic conductor. Pipes entering the buildings should be thoroughly connected to the protecting system, and if practicable insulated by rubber tubing or otherwise from the contiguous walls of metal.

Practically the same system of protection against lightning was adopted officially in Germany in 1906,[1] with a few modifications. The pillars in the outer zone were not so high, but from them was suspended a complete network of wires, which stretched all over the building at a height of about 3 metres above the roof. A second network was laid immediately on the roof. This system of double networks is called the Faraday cage, from a laboratory experiment devised by the great investigator. It has been adopted in South Africa also, but both there and in Germany buildings have been struck and destroyed, although they were provided with this very elaborate system of conductors. In June, 1910, three buildings were blown up simultaneously by lightning at the Schlebusch factory,[2] and in the same year the Faraday net failed in another German factory also. In February, 1911, there was a similar catastrophe at Modderfontein, whereby five men were killed. These disasters have brought into disrepute the system of suspending wires over the top of a building, because they appear to lead the flash into the house rather than away from it, as has now been shown experimentally by Rinckel[3] and Hagen[4] The prevailing opinion now is that the best protection is afforded by plain metal masts at some little distance from the building. These masts can be made at a small cost from ordinary gas-piping; they should be fitted at the top with metal points to assist the dissipation of induced charges of electricity.

It is a rule that the lightning conductors of danger buildings must be tested for electrical resistance at regular intervals to ensure that there is no break in the contacts. A direct flash of lightning can, of course, spring across enormous gaps, so that a small discontinuity in the conductor would probably be far less harmful than a sharp turn, but another function of the conductor is to dissipate gradually the induced charges that form on the surface of the earth when a thunder-cloud passes over it, and for this purpose continuous electric contact is essential.

It is expected by Bichel that the underground nitro-glycerine houses at Schlebusch will be far less liable to be struck by lightning.

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[1] *See S.S.*, 1907, p. 109.

[2] *See A.R.*, 1910, p. 38.

[3] *S.S.*, 1911, p. 141; 1907, pp. 109 and 277.

[4] *S.S.*, 1911, p. 162.

Frictional electricity. Dangerous charges of electricity may also be formed by the friction of non-conducting materials. The belts used for driving incorporating machines, for instance, are liable to become strongly electrified, especially in dry weather. To prevent this, at Waltham Abbey, the belts are dressed once a week with a mixture of glycerine and water, which makes the belts conduct and so prevents the accumulation of static charges of electricity. Dry gun-cotton is a material which is very liable to become electrified. All plant, on or in which it is placed, should therefore be connected to earth.

Interiors. The interior of danger buildings must be so constructed that so far as possible no iron or steel or gritty material is exposed. The thoroughness with which this rule is to be carried out depends to some extent on the nature of the explosives and of the operations to be carried out in the building. In nitro-glycerine houses the floors are generally made of lead sheet joined together by burning, and the walls are of wood. In gun-cotton stoves and mixing-houses, and other buildings in which explosive dust is liable to be formed, the walls and roof should be made so that they can be washed down with a hose, and should have no crevices in which material can lie. A smooth lining of zinc sheets soldered together serves the purpose well. In other buildings, and in magazines, the walls are generally lined with wood, and the floor is made of the same material; all crevices must be filled up; the nails used should be of copper, brass or other alloy; if iron nails or screws are used, they must be counter-sunk and covered with putty. Linoleum makes a very good covering for the floor, but it must be so laid that explosive dust cannot accumulate underneath it. Perhaps the very best material for the floor of ordinary danger buildings and magazines is asphalt, provided it be properly laid. Walls may also be made of neat cement painted over.

Barriers, etc. To prevent the introduction of grit into magazines and other danger buildings, the workers must change their boots as they enter, and in order that there may be no doubt as to which part is "clean" and which "dirty" there must be a wooden barrier erected, about 9 inches high, at the entrance to the building. Just outside the barrier there should be a lobby or porch in which the boots can be changed, and a small "clean" board on which the clean boots can stand whilst they are being put on. This board may with advantage be fastened with a hinge so that it can be tipped up when not in use. Those who have occasion to visit the danger building for only a short time usually put on clean over-boots with rubber soles, or preferably made entirely of rubber. The boots worn by the workers should also have soft soles with no iron nails. In some cases it has been found advisable to have copper rivets in the boots so as to "earth" the worker electrically, and so prevent the formation of sparks when he is dealing with substances like dry gun-cotton, which are liable to become electrified. In gun-cotton stoves, however, it is better not to wear any boots or shoes at all, but only an extra pair of woollen socks. In the East the natives as a rule go bare-foot, especially when indoors, consequently it is not necessary to provide special foot-gear for them to wear when they work in danger buildings, but a tub of water is placed just outside the barrier, and into this they have to dip their feet before entering the building, so as to wash off the grit.

Clothing.

All workers in danger buildings must wear special clothes which have no metal buttons or other metal parts, and no pockets. Where there is any danger of fire, the clothes should be made of wool, or be treated so as to render them inflammable. The clothes should not be allowed to become impregnated with explosive or inflammable or oxidizing material. The lives of the workers may be jeopardized if these precautions are not observed. Due provision must be made, by searching or otherwise, that no matches, pipes or other dangerous articles are introduced into a danger building.

Small magazines.

The principal regulations in force in England for small and moderate-sized stores and magazines for explosives are given in Appendix E of the *Guide to the Explosives Act*. Messrs. Curtis's and Harvey have issued a pamphlet, showing how these regulations can be carried out effectively and inexpensively, and giving full and detailed instructions for the erection of the buildings. The U.S. Bureau of Mines has also given instructions for the erection of magazines in the *Primer on Explosives for Coal-Miners* (Washington, 1911), and in Technical Paper 18 on "Magazines and Thaw-Houses for Explosives" (Washington, 1912), and the Du Pont Co. have given illustrations of buildings in their pamphlet on "High Explosives." The Bavarian Government also has issued instructions concerning this matter.[1]

In England explosives are not allowed to be stored underground in mines, but on the Continent small stores are permitted, and experiments have been carried out to test various methods of preventing the communication of explosions from such stores to others and to the mine.[2]

Thaw-houses.

Thaw-houses are required for thawing frozen nitro-glycerine explosives, when they have become frozen. In America the thawing is often carried out by placing the case of explosive within a closed box, which is embedded in fresh stable manure. This method of thawing is rather slow, however, and the temperature may rise to a dangerous height, 150° F., for instance. If practicable, the explosive should be warmed in a special house heated to about 100° F. (38° C.) by means of warm-water pipes, which preferably should not be brought into the building itself, but placed in a low recess just outside, communicating with it by means of an opening at floor level. It is still better not to allow the explosive ever to become frozen, but to keep the magazine itself at a temperature of 15° or 20° C. winter and summer.

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[1] *See S.S.*, 1911, p. 35.

[2] *See* J. Sauer, *S.S.*, 1907, p. 112; W. Serlo, *S.S.*, 1907, p. 114; Heinhold, *S.S.*, 1911, p. 195; *P. et S.*, vol. xvi., p. 206.

Tropical magazines.

In hot climates explosives containing nitro-cellulose or nitro-glycerine should be kept as cool as possible, because at high temperatures they deteriorate rapidly. This applies especially to the smokeless powders used for military and naval guns, as they have to be stored for much longer periods than commercial explosives. The magazines should therefore be specially constructed so as to keep as cool as possible, especially during the hot weather. If constructed of heavy masonry there is very little variation of temperature during the twenty-four hours, and this is of advantage. The magazine should only be ventilated during the night or the very early morning, when the temperature of the external air is lowest. In places where there is a large annual range of temperature considerable advantage is obtained by covering the magazine with earth as in Fig. 141. Where the quantities of explosive stored are sufficiently large, the magazines may with advantage be kept cold artificially, by circulating through them air cooled by means of a refrigerating plant. When this is done, the magazine must be insulated thermally by means of a layer of about 6 inches of slag wool, or other suitable material, applied to the walls, ceiling and floor.

Conveyance of explosives.

The regulations for the conveyance of explosives by carriage or boat in Great Britain are given in the *Guide to the Explosives Act*, p. 215. The railways have their by-laws. Some of the rules of the German State Railways are given in Appendix I. Methods for loading and staying packages of explosives in railway cars are described in detail by the American Bureau of Explosives in their pamphlet No. 6.[1]

Ship's magazines.

On board ship the explosives carried must necessarily be in close proximity to the crew and the other cargo. A wooden compartment is constructed well away from the boilers, steam-pipes, and all materials that could have an injurious effect.[2] On warships there are, of course, regular magazines forming part of the design of the vessel. There have been a number of cases in which ships have been destroyed by the spontaneous ignition of the smokeless powder on board, and since the *Jéna* catastrophe in 1907 practically all warships have had their magazines kept cold by means of refrigerating plant.

Naval catastrophes.

One of the most serious dangers to be guarded against in the storage of explosives is spontaneous ignition. Fires due to the ignition of deteriorated smokeless powders have been fairly numerous. Some of those that have occurred on board warships have been very disastrous. In September, 1905, the Japanese battleship *Mikasa* was destroyed in this manner in Sasebo harbour, and 599 lives were lost. The Brazilian warship *Aquidaban* sank in the port of Jacare, Rio de Janeiro, in January, 1906, with the loss of 213 lives. The French battleship *Jéna* blew up in March, 1907, in Toulon harbour,

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[1] Also in *Bureau of Explosives Annual Report*, No. 4, p. 73, 1911.

[2] *See* Memorandum of the Board of Trade relating to the Carriage of Dangerous Goods and Explosives in Ships.

killing 114 men. Another Japanese ship, the *Matsushima*, was lost off the Pescadores in March, 1908, together with 141 lives, apparently in consequence of the spontaneous ignition of the cordite on board. The French battleship *Liberté* was entirely destroyed in Toulon harbour in September, 1911, and 204 men were killed, 136 injured severely, and 48 slightly. In 1915 the Italian warship *Benedetto Brin* was destroyed apparently through the same cause.[1] These catastrophes are only some of the most serious. In addition there have been very many other cases of ignition, which, however, have fortunately not extended to the whole of the contents of the magazine, and consequently the damage has not been so serious. There have also been many cases of spontaneous ignition in magazines on land: in some cases the magazines have been entirely destroyed, together with surrounding objects; in other cases the ignition has not spread, and the damage has been trifling. A study of these cases leads to important conclusions as to the precautions to be taken to prevent a spontaneous ignition of smokeless powder leading to a destructive explosion. The total destruction of the *Jéna* was due to the spread of the flames from a magazine containing smokeless powder (Poudre B), which had ignited spontaneously, to one containing black powder, which then exploded. The loss of the *Matsushima* was apparently due to the same cause, and explosions of land magazines have in some instances been brought about in the same way, as, for instance, that of Batuco in Chile in March, 1908.[2] Gelatinized smokeless powders themselves hardly ever explode unless very strongly confined, and the larger sizes, which are used for ordnance, will only burn, however fierce the heat may be. The first deduction is therefore that smokeless powders should be stored quite separately from black powder and all other explosives that are liable to explode when ignited. Gunpowder is no longer used for the propulsive charges of naval guns, so that no ships can in future be destroyed in exactly the same way as the *Jéna* and the *Matsushima* were. The explosion on the *Liberté* was, however, much more violent, and men were killed several kilometres away by flying debris. There can be no doubt that this was due to the intense conflagration of the smokeless powder having caused the detonation of the high explosive shell filled with Mélinite (picric acid). Unfortunately it is not always possible on board ship to keep the shell very far away from the powder magazines, and consequently reliance must be placed on other precautions—refrigerating the magazines and thorough periodical inspection of the powder.

Gas explosions

Although there is no recorded case where smokeless powder has itself exploded after igniting spontaneously in a magazine, yet in a number of instances the ignition has been accompanied by explosive phenomena of a comparatively mild kind. When smokeless powder deflagrates in the absence

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[1] *See* Capt. Persius, *Berl. Tageblatt*; *S.S.*, 1915, p. 276.

[2] *See S.S.*, 1909, p. 265.

of air, the products consist largely of combustible gases. Berthelot gives the following figures for the products formed when nitro-glycerine and gun-cotton are ignited by means of a hot wire, and allowed to burn at a pressure about equal to that of the atmosphere:[1]

	Nitro-glycerine	Gun-cotton
NO	48·2	24·7
CO	35·9	41·9
CO_2	12·7	18·4
H_2	1·6	7·9
N_2	1·3	5·8
CH_4	·3	1·3
	100	100

The composition of the products will, of course, depend on that of the powder and also of the resistance offered by the package, that is, of the pressure under which the deflagration proceeds, but there will always be a large proportion of combustible gases, and these when they mix in certain proportions with the air of the magazine form an explosive mixture, which may be ignited by coming in contact with the burning contents of the case. In some cases the effects can only be explained by assuming that a gas explosion occurred. Similar phenomena have been observed, when spontaneous ignitions have occurred in stores of celluloid, the principal constituent of which is nitro-cellulose, and Will has come to the same conclusion as to the cause.[2] Those who have to do with the storage of gelatinized smokeless powders should therefore bear in mind that in the case of a spontaneous ignition far more serious damage may be caused by a gas explosion than by the ignition itself; moreover, if other explosives are stored in an adjoining compartment, the gas explosion, by blowing down the partition between, may lead to the explosion of these explosives, and so produce a widespread disaster. In the confined space on board ship such a gas explosion is likely to have very serious results. In the very full reports concerning the *Iéna* disaster there is distinct evidence that there was a gas explosion before the black powder went off. It might, perhaps, be possible to guard against the results of such an explosion on board warships by making the magazines of such strength that the walls, floors and roofs would withstand the pressure produced.

Spontaneous ignition.

The spontaneous ignition of smokeless powders, and of other explosives containing nitro-cellulose and nitro-glycerine, is due to rapid decomposition raising the temperature up to the ignition point. In decomposing, these substances give off oxides of nitrogen, which accelerate the decomposition, especially if nitric acid be formed by reaction with oxygen and water. The

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[1] *Explosives and their Power*, pp. 283, 289.

[2] *See Mitteilungen aus der Centralstelle*, Heft 5, Feb. 1906.

decomposition may thus proceed faster and faster, until it is sufficiently rapid to cause ignition. It is for this reason that substances, called stabilizers, are added to smokeless powders to combine with the oxides of nitrogen as they are evolved, and remove them from the sphere of the reactions. For a similar reason the magazines are kept cool, to reduce the velocity of the reactions of decomposition. Smokeless powders in the great majority of cases do not explode when they are ignited. If, however, there be a very large quantity present, and the powder be of small size, the burning may proceed with increasing violence until at length an explosion occurs. There is far more danger of an explosion if there be also present in the magazine dynamite or ungelatinized gun-cotton or other explosive that is liable to explode when ignited.

Repair of danger buildings

Before the interior of any danger building is repaired all explosive should be removed, and the building thoroughly washed out and inspected. Similarly any plant removed from the building must be cleaned inside and out. Nitro-glycerine should be removed from all surfaces with acetone or caustic soda. When buildings are to be demolished similar precautions must be taken, especially in the case of dusty explosives such as gunpowder. If it can be destroyed by water, as in the case of gunpowder, the roof may be removed and the rain allowed to wash the interior thoroughly, or a hose may be played on the structure inside and out. The space under the floor and between the joists should also be seen to. Minor repairs to the outside of building may sometimes be carried out without emptying it, provided that due precautions be observed.

Warnings.

The U.S. Bureau of Mines has issued the following warnings concerning the treatment of explosives in magazines: [1]

Don't store detonators with explosives.

Don't open packages of explosives in a magazine.

Don't open packages of explosives with a nail puller, pick or chisel, but with a hard wood wedge and mallet outside the magazine and at a distance from it.

Don't store explosives in a hot damp place.

Don't store explosives containing nitro-glycerine so that the cartridges stand on end.

Don't repair a magazine until all the explosives have been removed from it.

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[1] *Miners' Circular*, No. 6.

CHAPTER XXXVIII

STABILITY

Rate of decomposition . Action of micro-organisms : Foreign particles : Stabilizers : Ureas : Amines : Mineral jelly : Phenanthrene : Amyl-alcohol : Aromatic ethers, etc.

Rate of decomposition

THERE is no problem connected with modern explosives more important or more elusive than that of their stability. Black powder, and other similar mixtures of inorganic nitrates with combustible materials, can be stored indefinitely without suffering perceptible deterioration, provided that they are kept dry; picric acid, nitro-toluenes and other aromatic nitro-compounds are also very permanent. Nitro-celluloses, nitro-glycerine and similar substances, on the other hand, decompose to a perceptible extent even at the ordinary temperature, and the rate of decomposition increases rapidly with rise of temperature. This was not suspected at first, but Poudre B, introduced into the service in 1886, showed signs of decomposition eight years later.[1] The researches of Will[2] and Robertson[3] have established the fact that there is a certain minimum rate of decomposition of nitro-cellulose depending on the temperature and the degree of nitration. The presence of certain impurities in the nitro-cellulose may increase this rate considerably, but no amount of purification will reduce it below the "limit rate." The presence of oxides of nitrogen accelerates the decomposition, hence it is necessary to remove them as fast as they are formed by a current of inactive gas, when the rate is being determined. Sulphuric and other acids also act as catalytic agents in accelerating the reaction.

To express the variation of the rate of decomposition with temperature Will proposed the formula $log\ N = a + b \times 0{\cdot}9932^t$, and for the nitro-cotton with which he was experimenting he found $a = 8{\cdot}842$ and $b = -22{\cdot}86$, N being the number of milligrammes of nitrogen evolved by 2·5 g. in ¼ hour.

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[1] Buisson, *Problème des Poudres*, p. 109.

[2] *Mitteilungen aus der Centralstelle*, Heft 2, Dec. 1900, and Heft 3, July, 1902.

[3] *J. Soc. Chem. Ind.*, vol. i., 1902, p. 828.

But the facts are represented equally well, or better, by the simpler equation

$$\log V = Kt + C$$

or

$$V = k^t \times c,$$

where V is the velocity of the reaction, t the temperature, k and c constants, and K and C their logarithms. Equations of this form were suggested by Berthelot many years ago.[1] The constant C depends upon the state of purity of the substance, the degree of nitration and the units in which the velocity V is measured. K depends only on the nature of the substance. For nitro-cotton, according to Will's results, the rate of decomposition is doubled for every rise of 5° C. Therefore $K = \frac{\log 2}{5} = 0{\cdot}0602$, and $k = 1{\cdot}149$. Robertson obtained practically the same value in the case of nitro-glycerine.[2] For gun-cotton thoroughly stabilized $C = \bar{9}{\cdot}70$, and for nitro-glycerine $\bar{8}{\cdot}785$, if V is the number of milligrammes of nitrogen evolved per hour by 1 gramme.

Gelatinized nitro glycerine high explosives are liable to deteriorate in this way, and in several instances the blowing up of magazines has been traced to this cause. Many consignments of such explosives have been condemned after shipment from this country to Australia on account of their failure to pass the heat test on arrival. But it is in connexion with smokeless powders for military and naval use that most attention has been drawn to the gradual deterioration of these explosives, and their liability to ignite spontaneously. Some of the principal disasters due to this cause were mentioned in the last chapter. As regards the variation of the rate of deterioration with temperature, the French authorities have adopted the rule that an hour at 110° is equivalent to a day of 75° and a month at 40°,[3] which gives values for K of 0·0394 and 0·0423. On the other hand, in a British War Office publication, the *Regulations for Army Ordnance Services*, Pt. II, paragraph 359, 1908, a Table is given based on an increase in the rate of deterioration for every 5° C. of 1·7 times, which gives for K a value of 0·0461. The French figures are for nitro-cellulose powder, whereas the English ones are for cordite, and they have been deduced from data of quite a different kind, so that a close agreement could not be expected in a matter in which it is so difficult to attain accuracy, but it seems to be clear that the rate of deterioration is less than doubled for a rise of 5° C.

The rate of deterioration or, in other words, the magnitude of the constant, C, depends upon the presence or absence of various substances in the smokeless powder or other explosive. Normal nitro cotton thoroughly purified in accordance with the methods given in Chapter XIII deteriorates less rapidly, and

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[1] *Ann. Chim. Phys.*, 1862, p. 110.

[2] *Seventh Inter. Cong. Appl. Chem.*, 1909, vol. iii*b*, p. 95.

[3] *P. et S.*, vol. xv.

therefore is more stable, than the nitric esters of allied substances such as oxy-cellulose or pecto-cellulose. Some of the unstable products are removed by treating the nitro-cellulose with alcohol.

Berl and Delpy[1] examined some of the material removed from commercial nitro-cotton in the process of alcoholizing, and found that it contained about 10 per cent. nitrogen and had a very low temperature of ignition. When mixed with good nitro-cotton it did not affect its temperature of ignition to a perceptible extent, however: a fact which confirms the opinion that the temperature of ignition is not a satisfactory indication of stability. F. Langenscheidt[2] has also examined the alcohol extract. He found that extraction improved the Bergmann and Junk test from 2·36 to 2·0 c.c. in one case, and from 2·4 to 2·2 in another. The material recovered from solution gave a test of 3·17 c.c., but had been dried for several months at the ordinary temperature, and may have already given off some nitrogen. When dried rapidly it gave a heat test of 5 minutes at 80°. He found that the alcohol from the alcoholizing process contained 5 to 7 grammes of nitro-cellulose per litre.

The rate of deterioration is increased by the presence of strong acid, which hydrolyses the compounds. The acid is not consumed in the reactions that occur, on the contrary the explosive becomes more and more acid by the formation of nitric acid. The reaction is therefore auto catalytic. The reactions that occur during the storage of smokeless powders are very complex: the solid and liquid products formed were discussed in Chapter XIII, but the mechanism of the change is apparently dependent very largely on the presence of the oxides of nitrogen, which are gases. It was found by Robertson and Napper[3] that of the nitrogenous gases evolved by gun-cotton at 135° under the conditions of the Will test, about 40 per cent. consists of nitrogen peroxide NO_2, and the remaining 60 per cent. is mostly nitric oxide NO. From nitro-glycerine the whole of the nitrogen is evolved in the form of NO_2.[4] If the gaseous products remain in contact with the gun cotton, the NO_2 is reduced to NO, and the gun-cotton is correspondingly oxidized with evil effects on its stability. Nitro-glycerine is apparently not oxidized so readily, and this may be one reason for the greater stability of nitro-glycerine powders. If air be present, the NO is at once oxidized again to NO_2, and unless the nitrous gases are removed in some way, these oxidations and reductions will continue until all the oxygen present has been exhausted. This oxidation of nitro-cellulose proceeds most rapidly if the conditions be such that there is a continuous but small supply of oxygen: if the uncompressed material be exposed freely to the air, the nitrous oxides diffuse away before they have been able

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[1] E. Berl and M. Delpy, *S.S.*, 1913, p. 129.

[2] *S.S.*, 1914, p. 54.

[3] *Trans. Chem. Soc.*, 1907, vol. 91, p. 764.

[4] Robertson, *Seventh Inter. Cong. Appl. Chem.*, 1909, vol. iii*b*, p. 95.

to do much harm. Thus it has been observed that if porous nitro-cellulose be compressed into compact blocks under a pressure of 3600 kg. per square cm. (23 tons per square inch), and heated at 110° under the conditions of the Vieille test, it gives a result of only about 10 hours, whereas the same material merely moulded under a pressure of 400 kg. per square cm. (2½ tons per square inch) gives a result of about 100 hours.[1] In the latter case the oxides of nitrogen can diffuse away, but in the former they do not diffuse so fast as they are formed, and yet the blocks are sufficiently porous to allow oxygen to diffuse into them.

If air be excluded, the NO is further reduced to innocuous compounds, nitrogen suboxide (laughing gas, N_2O) and nitrogen. Thus it was found by Vieille[2] that after heating Poudre B for twenty days at 75° in an atmosphere of carbon dioxide, the residual gas after absorption of the carbon dioxide had the following composition :

CO	7
NO	13
N_2O	8
N_2	72

The composition of the gases that accumulated in submarine mines containing compressed gun-cotton, which had been hermetically closed and immersed in water for seven or eight years, was found to be :

O_2	0·3	–	0·33
CO_2	2·1	2·3	2·09
CH_4	0·5	0·85	0·43
H_2	6·5	5·93	6·52
N_2O	1·5	1·0	1·42
N_2	88·9	89·05	88·61
	99·8	99·13	99·40

The gases were collected over water.[3]

The fact that nitro-glycerine powders do not become porous, even when the solvent has all escaped, renders them less liable to attack by atmospheric oxygen. Poudre B, on the other hand, is somewhat porous even when new.

In the presence of water nitric peroxide forms nitric acid, which, as already stated, has a strong hydrolytic decomposing effect on nitro-cellulose and nitro-glycerine, especially the latter.[4] The explosives always contain several tenths per cent. of water which they have absorbed from the atmosphere ; moreover, water is one of the normal products of the deterioration of the

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[1] *P. et S.*, vol. xv., 1910, p. 64.

[2] *P. et S.*, vol. xv., p. 92. *See also* E. Berger, *Bull. Soc. Chim.*, 11, 1912, p. 1.

[3] *Loc cit.*, p. 63.

[4] *See* Silberrad and Farmer, *Trans. Chem. Soc.*, vol. 89, 1906, p. 1759.

substances. The moisture plays an important part in the decompositions, and one of the greatest problems in devising satisfactory stability tests lies in the difficulty of regulating the amount of water present in the material which is undergoing the tests. In the entire absence of water, the oxides of nitrogen only assist the oxidation of the material; no hydrolysis can occur. On the other hand, if the amount of water present be very large, the acids are diluted so much that their action is much diminished. There is an intermediate amount of moisture which causes a maximum of decomposition. Nitric acid, although injurious, is liable to be destroyed by reacting with the nitro-cellulose: moreover, it is volatile and consequently may escape altogether. Sulphuric acid, on the other hand, is practically permanent, and so unless there be some basic substance present, which will neutralize it, it has a much worse effect. It is, no doubt, for this reason that the presence of sulphuric esters is so very injurious, for in course of time they lead to the formation of sulphuric acid. The organic acids, formed in the deterioration of the explosives, are so weak in their action that they are not very harmful.

Action of micro-organisms.

Moist nitro-cellulose is liable to be attacked by a fungus which turns it black and reduces its heat test, but apparently this only occurs where the nitro-cellulose is in contact with paper or other organic matter. For this reason compressed gun-cotton slabs are generally impregnated with carbolic acid. In Germany mercuric chloride is often added to prevent the growth of fungi and bacteria, but in England this is not allowed, as it masks the heat test.

Foreign particles.

The presence of foreign particles in explosives may diminish the stability, thus Thomas at the Fifth International Congress of Applied Chemistry (Berlin, 1903) recorded a case in which the accidental imbedding of the head of an iron nail caused the spontaneous decomposition of a nitro-glycerine powder. Partly nitrated foreign matter, derived from impurities in the cotton used, has a deleterious effect too, as also have various other substances. Therefore all extraneous bodies should be eliminated as far as practicable during manufacture, especially particles of iron, such as are liable to be detached from the knives of the beaters. These can be removed almost entirely by passing the pulp between the poles of a powerful electro-magnet, as has been done for many years past in the manufacture of the better classes of paper.

Stabilizers.

The idea of adding substances to these explosives to combine with the acid products of decomposition, and so prolong the life of the material, occurred at an early date. Von Lenk treated the gun-cotton with a solution of sodium silicate and then washed it. It was shown by Abel [1] that the beneficial action was due to the precipitation of calcium carbonate in the fibres by the interaction between the sodium silicate and the calcium salts in the water used. When gun-cotton is stabilized by boiling in hard water, calcium carbonate

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[1] *Phil. Trans. R.S.*, 1867, p. 181.

is similarly precipitated in it to the extent of several tenths per cent., and it has been found that this is necessary for the stability of the material, if it is to be stored for a considerable period of time. When very soft water is used, it has been found necessary, in some instances, to add carbonate.

Strong alkali in aqueous solution has a much greater hydrolytic action on nitro-cellulose than acid. Silberrad and Farmer found that caustic baryta acted 480 times as fast as nitric acid under the same conditions.[1] Therefore only such alkaline substances should be employed as are practically insoluble in water. The carbonates of calcium and magnesium are those that are generally used; to nitro-glycerine blasting explosives 1 or 2 per cent. of these substances are often added. Ammonium carbonate has also been used for this purpose; it is such a weak base that it cannot have a very powerful hydrolytic action, in spite of its ready solubility in water, but it is objectionable on other grounds: it is volatile and deliquescent, and it dissociates into carbon dioxide and ammonia, which reacts with the nitric esters and accelerates their decomposition.

On storage the alkali gradually becomes neutralized, being converted mostly into nitrate, together with some nitrite, but a few tenths per cent. of calcium carbonate will enable a well-prepared gun-cotton to withstand even tropical temperatures for a great many years.

Although gun-cotton containing calcium carbonate is more stable than that containing none, it gives a lower heat test. This is apparently due to the fact that at the temperature of the test, the calcium nitrite present decomposes more readily than the gun-cotton, giving off oxide of nitrogen, which affects the test paper. By washing such a gun-cotton with distilled water, so as to remove soluble salts, the heat test is improved.

Ureas.

Basic compounds, to neutralize the acids formed, are not the only substances that have been added to explosives to increase their stability. There are also various other substances, which can react with the oxides of nitrogen to form innocuous compounds. Amongst the substances that have been studied in this connexion are urea and its derivatives, carbamide, aniline, diphenylamine, nitroso-diphenylamine, nitro-guanidine, trinitro-naphthalene, vaseline, camphor, castor oil, phenanthrene and rosaniline. Urea has been used extensively as a stabilizer for celluloid,[2] and was at one time a constituent of American military powders. It reacts with nitrous acid to form carbon dioxide and nitrogen:

$$CO(NH_2)_2 + 2HNO_2 = 2N_2 + CO_2 + 3H_2O,$$

but it also attacks the nitro-cellulose, and is no longer employed as an ingredient of explosives. By substituting organic radicles for the hydrogen atoms it is stated that the injurious action is prevented. J. Stevens found diethyl-diphenyl-urea, $CON_2(C_2H_5)_2(C_6H_5)_2$ and tetraphenyl urea $CON_2(C_6H_5)_4$ the

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[1] *Trans. Chem. Soc.*, 1906, p. 1759.

[2] *See* Worden, *Nitrocellulose Industry*, p. 596.

best.[1] It is stated that dimethyl-diphenyl-urea, called Centralite, is being tried in France as a surface gelatinizing agent.[2] The use of these compounds for this purpose has been patented by Claessen.

Amines. Aniline $C_6H_5NH_2$ was formerly used in Italy as an addition to Filite. With nitric peroxide it forms diazo-benzene nitrate, which, however, is unstable and breaks down into phenol and nitric acid. By replacing another of the hydrogen atoms attached to the nitrogen more satisfactory stabilizers are produced.

The use of diphenylamine $(C_6H_5)_2NH$ as a stabilizer was patented by Nobel in 1889, and it has been used in Germany for this purpose for some twenty years. As there do not seem to have been any serious spontaneous ignitions of smokeless powder in that country, the fact is significant. Diphenylamine has also been adopted by Italy, Sweden, and Spain. In France it was under trial for many years, and since October, 1910, it is added to all Poudre B.[3] In the United States 0·45 per cent. is incorporated with the nitro-cellulose smokeless powder,[4] and it is claimed officially that the life of the powder is thereby increased from six or seven years to twenty years or more.[5] Secondary and tertiary amines, such as di- and triphenyl-amine with nitrogen peroxide form nitro- and nitroso-compounds, which are comparatively stable. There is, however, considerable field for research to ascertain which of the many available amine derivatives or other compounds are the best stabilizers.

From the results of a few heat tests carried out by Guttmann's method, Carneiro concluded that diphenyl-amine is injurious to the stability.[6] This difficult question cannot be settled so easily, however. It is only by keeping quantities for periods extending over several years, under conditions resembling the most severe that are likely to be met with in actual storage, combined with chemical investigations of the changes that take place, and stability tests at intervals of time, that definite conclusions can be reached, and even then the results must be interpreted with care. Such trials have been conducted in France and have given favourable results, and the same has been the case in America also. Vieille and Marqueyrol have found that 5 or 10 per cent. of diphenyl-amine attacks smokeless powder to a notable extent at 110°, but 2 per cent. has practically no action upon it. An advantage of diphenyl-amine is that its nitroso- and nitro-compounds give definite reactions that may be utilized to follow the deterioration of the powder.

Mineral jelly. Mineral jelly, which was originally added to cordite for quite other reasons,

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[1] U.S. Pat. 593,787 of 1897; Russ. Pat. 12,649 of 1907.

[2] Florentin, *La Technique Moderne*; *S.S.*, 1913, p. 32.

[3] Florentin, *La Technique Moderne*; *S.S.*, 1913, p. 7.

[4] Worden, *Nitrocellulose Industry*, p. 907.

[5] Report *U.S. Joint Army and Navy Board*, *U.S. Naval Institute Proceedings*, March, 1912.

[6] *S.S.*, 1909, p. 30.

has been found to have a great stabilizing effect. It is a very complex mixture of hydrocarbons, many of which are unsaturated and are able to combine with the oxides of nitrogen. Also by forming an impervious layer on the outside of the sticks, it preserves the explosive from oxidation by the air.

Phenanthrene. Spica has proposed the addition of phenanthrene $C_{14}H_{10}$ to smokeless powders to improve the stability, and also to reduce the temperature of explosion.[1]

Amyl-alcohol. It was found in France that the presence of residual solvent in Poudre B added to its chemical as well as its ballistic stability. To some extent the increase in chemical stability is no doubt due to reaction of the alcohol with the oxides of nitrogen, with formation of nitrous and nitric ether, but its effect is apparently due principally to its preventing the powder becoming degelatinized and consequently more porous. The presence of solvent thus impedes the oxidation of the nitro-cotton. As ethyl-alcohol is inconveniently volatile, it was partly replaced by amyl-alcohol, which has a higher boiling-point. Of 2 per cent. added to powders of small size about 1 per cent. remained in the dried powder, and of 8 per cent. added to large naval powders about 4 per cent. remained. Amyl-alcohol has now been replaced by diphenyl-amine in the French service.

Aromatic ethers, etc. Nathan, Rintoul, and Baker, in a series of patents (12,742 to 12,746 of 1912), have pointed out that it is necessary that a stabilizer be capable of being incorporated uniformly into the smokeless powder, and that it shall not separate out during the drying. They have found several different classes of substances which are suitable in this respect and react rapidly with the oxides of nitrogen: aromatic ethers, such as ethyl-naphthyl-ether $C_{10}H_7.O.C_2H_5$; derivatives of carbamic acid, such as methyl-phenyl urethane; urea derivatives, such as ethyl-phenyl urea; and anilides and derivatives of other acid amides, aceto-ortho-toluidide $CH_3.C_6H_4.CH_2.CO.NH_2$, for instance. Of any of these 5 per cent. may be introduced into cordite MD in the place of the mineral jelly.[2]

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[1] *S.S.*, 1912, p. 129.

[2] *See also* Eng. Pats. 4940 and 4941 of 1913.

CHAPTER XXXIX

STABILITY TESTS

Trace tests. Abel heat test : Heat Test Committee : United States directions : In France : Precautions : Significance of heat test : Other trace tests : Fume tests : Vieille test : German 135° test : Waltham Abbey silvered vessel test : Surveillance test : Fuming-off test : Quantitative tests : Will test : Bergmann and Junk test : Sy's test . Other quantitative tests : Calorimetric test : Light tests : Examination of stabilizer Diphenyl-amine

In the early days of the manufacture of nitro cellulose there were no methods known for distinguishing readily a stable from an unstable explosive, and the result was a series of devastating explosions which practically put a stop for a time to the new industry. It was only after Sir Frederick Abel had introduced the " heat test " that it was possible to carry on the manufacture of modern explosives with safety. Although this test has many imperfections, and a large number of other tests have been proposed to replace it, it is still the one that is most used, as it is very simple and easy to carry out, and the other tests are also not free from faults.

Classes of tests

Nearly all the stability tests that have been proposed depend on the detection or measurement of the nitrogen oxides given off when the explosive is heated to a more or less elevated temperature. The first class of these tests is that of the so-called " trace tests," in which the explosive is heated at a moderate temperature, such as 160° or 180° F. (70° or 80° C.), and the time taken to colour a very sensitive test-paper or solution is observed. The Abel test belongs to this class. The second division is that of the " fume tests," in which the sample is heated at a considerably higher temperature, 100° to 135°, and the time noted until it commences to fume, or until it affects some less sensitive reagent, such as litmus-paper. The third class, that of the " quantitative tests," comprises those in which the gun-cotton is heated at a fixed temperature within about the same limits as those of the " fume tests," and measurements are made of the amount of the oxides of nitrogen or the total products of decomposition given off in a fixed period of time.

The Abel Heat Test

The following are the principal appliances required for this test as laid down by the British Home Office :

Argand gas burner or Berzelius spirit lamp if gas is not available.

Needle for piercing heat test-papers.

Test-tubes 5$\frac{3}{8}$ to 5$\frac{1}{2}$ inches long, and of such a diameter that they will hold from 20 to 22 c.c. of water when filled to a height of 5 inches.

India-rubber stoppers, size no. 4, fitting the test-tubes and carrying an arrangement for holding the test paper, viz. a narrow glass tube or rod passing through the centre of the stopper, and drawn out so as to form a hook, or terminating in a platinum wire hook (Fig. 142).

A *water-oven*, measuring inside about 9 inches each way, with wire gauze shelves about 3 inches apart.

A *thermometer.*

A *clock or watch.*

Special Water-bath. This consists of a spherical copper vessel, A (Fig. 143), of about 7$\frac{7}{8}$ inches diameter with an aperture of about 5$\frac{7}{8}$ inches; it has a loose lid of sheet copper about 6 inches in diameter, and rests on a tripod stand, which is surrounded by a screen of thin sheet copper; within the latter is placed the Berzelius or Argand burner, with copper chimney. The lid has seven holes, one to receive a thermometer and the other six to receive the test-tubes containing the explosives to be tested. Around each of the holes 1 to 6, on the underside of the lid, are soldered three pieces of brass with points slightly converging. These serve to hold the test-tubes in position and allow them to be easily removed.

A *Nest of 2 Sieves* with holes drilled in sheet copper (Fig. 144). The holes in the top sieve have a diameter equal to 14 BWG; those in the second sieve are equal to 21 BWG. The lower sieve fits into a box also of sheet copper, and the upper sieve is closed with a copper lid. There are standard patterns of sieves and bath, which can be obtained from the usual dealers in chemical apparatus.

Mill. This also is of standard pattern and can be obtained from the same sources (Fig. 145).

Cutter for cutting up Cordite MD and other tough materials.

The *test-paper* is prepared as follows: 3 g. of white maize starch (cornflour) previously washed with cold water are added to 250 c.c. of distilled water, the mixture stirred, heated to boiling and kept gently boiling for ten minutes; 1 g. of pure potassium iodide (recrystallized from alcohol) is dissolved in 250 c.c. of distilled water. The two solutions are thoroughly mixed and allowed to get cold. Strips or sheets of the best white English filter-paper, weighing air-dry 4·1 to 4·6 g. per 100 square inches (645 sq. cm.), previously washed with water and dried,[1] are dipped into the solution thus prepared,

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[1] As some English filter-paper has been found to contain some substance soluble in acetic acid, which liberates iodine from potassium iodide, the Home Office authorities now find it advisable to wash the filter-paper twice with dilute acetic acid, made by

and allowed to remain in it not less than ten seconds; they are then allowed to drain and dry in a place free from laboratory fumes and dust. The upper and lower margins of the strips or sheets are cut off, and the paper is preserved in well-stoppered or corked bottles *in the dark*. After preparation the papers should be kept (in the dark) for a month before being taken into use. After that, if kept carefully (in the dark), they will remain good for six months or longer, but they should be tested from time to time by putting on one of them a drop of dilute acetic acid, made by mixing 1 volume of acetic acid, B.P., with 4 volumes of distilled water. The freshly prepared paper and that which is still in good condition will give no coloration. In time, however, and soonest in a bright light, a drop of acid produces a brown or bluish coloration. A single hour of strong sunlight causes a marked effect. If the paper is unserviceable, the discoloration takes place at once; any discoloration taking place some time afterward may be disregarded.

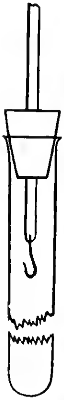

Fig. 142. Heat Test Tube (from *A.R.*, 1907, p. 107)

Fig. 143. Heat Test Bath (from *Baird and Tatlock's Catalogue*)

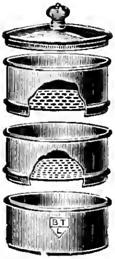

Fig. 144. Nest of Sieves

Fig. 145. Mill for Cordite

The dimensions of the pieces of test-paper used are about 20 mm. by 10 mm. (0·8 by 0·4 inches).

Standard tint-paper.

Standard Tint-paper. A solution of caramel in water is made of such

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mixing 1 part of the glacial acid with 10 parts of distilled water, wash all night in running tap water, rinse twice in distilled water, dry, and proceed as above (*A.R.*, 1907, p. 17).

strength that when diluted 100 times the tint of the solution equals that produced by Nessler reagent in 100 c.c. of water containing 0·000235 g. of ammonium chloride. With this solution lines are drawn by means of a clean quill pen on strips of filter-paper previously washed with distilled water to remove traces of bleaching matter and dried. When these marks are dry the paper is cut into pieces of the same size as the test-paper previously described, so that each piece has a line across it near the middle of its length. Only those strips are used in which the brown line has a breadth of from 0·5 to 1 mm. The standard tint-paper should be kept in a corked tube, and should not be exposed to the light except when actually in use.

Gun-cotton, compressed nitro-cellulose, tonite, etc.

Preparation of the Sample. In the case of gun-cotton compressed nitro-cellulose, tonite, etc., sufficient material to serve for two or more tests is removed from the centre of the block or cartridge by gentle scraping, and if necessary further reduced by rubbing through a sieve with a clean hard brush. The fine powder thus produced is spread out in a thin layer upon a paper tray 6 inches by 4·5 inches, which is then placed on one of the wire gauze shelves of the water-oven, which is kept as nearly as possible at 120° F. (49°). The sample is allowed to remain at rest for fifteen minutes in the oven, the door of which is left wide open. After the lapse of fifteen minutes the tray is removed, and exposed to the air of the room for two hours, the sample being at some point within that time rubbed upon the tray with a brush in order to reduce it to a fine and uniform state of division.

The English War Department method differs from this in specifying that after drying in the oven the gun-cotton shall be exposed for four hours instead of two.

Application of the Test. The water-bath is to be filled to within 0·25 inches of the edge. The thermometer is inserted through hole No. 7 of the lid so as to be immersed in the water to a depth of $2\frac{3}{4}$ inches, and the water is heated and maintained at a temperature of 170° F. (76·7°). When this temperature is reached 20 grains (1·3 g.) of the prepared gun cotton is weighed out, placed in the test-tube, and gently pressed down until it occupies a space of not more than 1·3 inch in the test-tube. A test-paper is affixed to the hook on the glass rod and moistened with distilled water mixed with an equal quantity of pure glycerine. The quantity of liquid used must only be sufficient to moisten about half of the paper. The cork carrying the rod and test-paper is then fixed into the test-tube, and the latter inserted into the bath to a depth of $2\frac{3}{4}$ inches. The test-paper is to be kept near the top of the test-tube, but free of the cork, until the tube has been immersed for about five minutes. A ring of moisture will about this time be deposited upon the sides of the test-tube a little above the cover of the bath; the glass rod must then be lowered until the lower margin of the moistened part of the paper is on a level with the bottom of the ring of moisture in the tube; the paper is now watched closely. The test is complete when the faint brown line, which makes its appearance on the line of boundary between the dry and moist portions of paper, equals in tint the line on the standard tint-paper.

The interval of time between the first insertion of the test-tube in the water at 170° F. and the production of the standard tint constitutes the test, and this interval of time must be *not less* than ten minutes, or the sample will not be considered to have satisfied the test.

According to the Home Office the glycerine and water mixture is to be applied to the upper edge of the test-paper by means of a camel's hair pencil; but according to the War Office instructions the thin rod-like prolongation of the stopper of a dropping bottle is to be used, and this is to be laid across the paper, which meanwhile is held at the lower end by means of forceps; the paper is placed on the hook after it has been moistened. If the quantity of liquid applied is so large that the edge of the moistened portion creeps down $\frac{1}{8}$ inch after the tube has been inserted in the bath, the test should be discarded.

These and other differences appear very trivial, but with such a very delicate test very slight causes produce differences in the results.

Schultze E C Powder and other sporting powders.

Schultze and E C Powders contain a considerable proportion of ungelatinized nitro-cellulose, and should be dried, exposed, and tested in the same manner as gun-cotton.

Other sporting powders and preparations containing nitro-cellulose, gelatinized or semi-gelatinized, are tested as follows:

If the preparation is in the form of small flakes or grains, as is the case with some rifle powders, 1·6 g. (25 grains) are weighed out into a test-tube. But if the pieces are larger, as in the case of cordite, they must be broken up and ground. Pieces $\frac{1}{2}$ inch long are cut from one end of all the sticks of cordite selected for the test, and in the case of the larger sizes of cordite each piece so cut is further subdivided into four portions. These cut pieces are then passed once through the mill, the first portion of material that passes through being rejected on account of the possible presence of foreign matter from the mill. The ground material is put on the top sieve of the nest and sifted. That portion which has passed through the top sieve and been stopped by the second is taken for the test. If the mill is properly set, the greater part of the ground material will be of the proper size.

Cordite and other rifle powders.

If too hard for the mill, the material may be softened by exposure to the vapour of acetone, or reduced to the necessary state of subdivision, by means of a moderately coarse rasp. Should the acetone vapour have rendered it too soft for the mill, it should be cut up into small pieces, which may be brought to any desired degree of hardness by simple exposure to air.

Explosives, which consist partly of gelatinized collodion cotton and partly of ungelatinized gun-cotton, are best reduced to powder by a rasp, or softened by exposure to mixed ether and alcohol vapour at a temperature of 33° to 39° (90° to 100° F.).

If the volatile matter in the explosive exceeds 0·5 per cent., the sifted material should be dried at a temperature not exceeding 140° F. (61°) until the proportion is not more than 0·5 per cent.

After each sample has been ground, the mill must be taken to pieces and carefully cleaned.

The War Office regulations, on the other hand, do not allow of softening the cordite with acetone vapour. Small pieces or slices about $\frac{1}{8}$ inch thick are cut off and passed through the mill, the first portion being rejected. The portion that passes through the first sieve, but is stopped by the second, is used for the heat and moisture tests, whereas the finer portion which passes through the second sieve is used for the rest of the analysis. The material used for the heat and moisture tests should not pass through the mill more than once, else there will be some loss of volatile constituents. It should be put at once into well-stoppered bottles and should not be touched with the hands.

No delay should take place between the grinding of the cordite and the carrying out of the test, and aeration should be avoided. The adjustment of the percentage of volatile matter to 0·5 is, therefore, directly contrary to the Service regulations, although recommended by the Home Office.

For the application of the test the Home Office instructions are as follows: The thermometer is fixed so as to be inserted through the lid of the water-bath (Fig. 143) into the water to a depth of 2·75 inches. The water is to be maintained at a constant temperature of 180° F. (82·2°). A test-paper is fixed on the hook of the glass rod, so that when inserted into the tube it will be in a vertical position. It is moistened with glycerine and water as directed above for gun-cotton. The cork carrying the rod and paper is fixed into the test-tube and the position of the paper adjusted so that its lower edge is about half-way down the tube, which is then inserted through one of the holes in the cover of the bath to such a depth that the lower margin of the moistened part of the paper is about 0·6 inches above the surface of the cover. The test is completed when the faint brown tint, which after a time makes its appearance at the margin between the wet and dry portions of the test-paper, equals in depth of tint the brown line drawn on the standard tint-paper. The time which elapses between the insertion of the test-tube into the bath at 180° F. and the completion of the test must not be less than fifteen minutes, according to the Home Office regulations.

No new cordite is accepted by the War Office unless it stands a heat test of thirty minutes at 180° F., but the test is carried out with papers that are less sensitive than those of the Home Office. Cordite, which has already been issued to the Services, is tested at 160° F. (71·1°).

Nitro-glycerine.

As nitro-glycerine by itself is not an article of commerce, the Home Office does not find it necessary to specify a test for it, but only for nitro-glycerine extracted from such materials as dynamite and for nitro-glycerine explosives. The War Office, however, specifies a test for the nitro-glycerine that is used in the manufacture of cordite. For this 6·5 g. (100 grains) are taken and passed through a neutral filter-paper to remove moisture. Of the filtrate 3·25 g. (50 grains) or 2 c.c. are introduced into a test-tube, and the test is carried out as in the case of cordite. It must give a test of at least eighteen minutes at 180° F.

Dynamite.

Nitro-glycerine explosives, from which the nitro-glycerine can be removed mechanically, must satisfy the following test laid down by the Home Office: This test, however, though looked upon at present as the most important, so far as testing the purity of the nitro-glycerine is concerned, is only one of several, which any given sample of nitro-glycerine preparation has to satisfy in order to establish its compliance with the definition in the Authorized List.

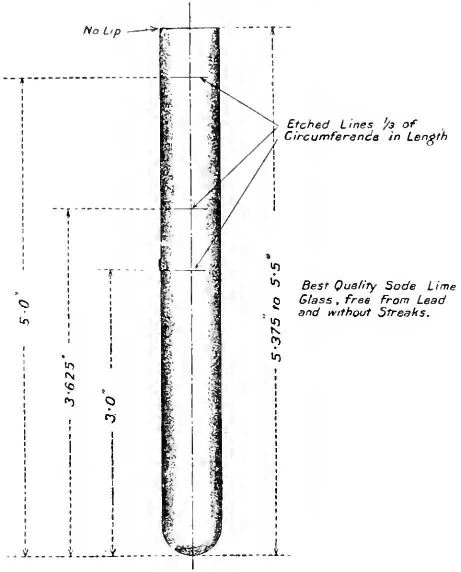
About 20 or 26 g. (300 or 400 grains) of dynamite, finely divided, are placed in a funnel 2 inches in diameter, which has previously been plugged with some freshly ignited asbestos. The surface is smoothed by means of a flat-headed glass rod or stopper and some clean-washed and dried kieselguhr is spread over it to a depth of ¼ inch. Water is next carefully dropped from a wash-bottle upon the kieselguhr, and when the first portion has been soaked up, more is added: this is repeated until sufficient nitro-glycerine has been collected in the graduated measure below. If any water should have passed through with the nitro-glycerine it should be removed with a piece of blotting-paper, and the nitro-glycerine, if necessary, filtered through a dry filter-paper.

Application of the Test. 3·25 g. (50 grains) or 2 c.c. of the nitro-glycerine are weighed into a test-tube in such a way as not to soil the sides of the tube, and the test is carried out as in the case of cordite, except that the temperature of the bath is 160° F. (71·1°). The nitro-glycerine will not be considered to have satisfied the test unless the time necessary to produce the standard tint is at least fifteen minutes.

Blasting gelatine, gelatine dynamite, etc.

3·25 g. (50 grains) of blasting gelatine are to be intimately incorporated with 6·5 g. (100 grains) of French chalk. This can be effected readily by working the two materials together with a wooden pestle in a wooden mortar. The French chalk should be of good commercial quality, and, after being carefully washed with distilled water and dried in a water-oven, it should be exposed under a bell jar to moist air until it has taken up about 0·5 per cent. of moisture. It should then be bottled for use, and with ordinary care the percentage of moisture will not alter much.

The mixture is to be introduced gradually into a test-tube of the dimensions prescribed above with the aid of gentle tapping on the table between the introduction of successive portions of the mixture into the tube, so that when the tube contains all of the mixture it shall be filled to the extent of 1·75 inches of its height. The test-paper is then to be inserted and the heat applied in the manner prescribed above. The sample tested is to withstand exposure to 160° F. (71·1°) for a period of ten minutes before producing a discoloration of the test-paper corresponding in tint to the standard tint-paper.



Tubes after Subjection for 3 Hours to a Steam Pressure of 50 lbs. per square inch and then Air dried, must not show more Cloudiness than the Standard Sample so treated. To carry out this Test, the Tubes are to be placed in an inverted position in an Autoclave and well clear of the Liquid.

FIG. 146. Heat Test Tube

(From First Report of Heat Test Committee, by permission of the Controller of H.M. Stationery Office)

Non-gelatinized nitro-glycerine preparations, from which the nitro-glycerine cannot be expelled by water, are tested without any previous separation of the ingredients, the temperature being, as above, 160° F. and the time seven minutes.

Heat Test Committee.

As there was much uncertainty as to the exact way in which the test was to be carried out, and the procedure of the Home Office was different to that of the War Office, a joint Committee was appointed in April, 1909, representing the Home Office, the Admiralty, the War Office, and the explosives trade, to make investigations with a view to obtaining greater uniformity in the methods

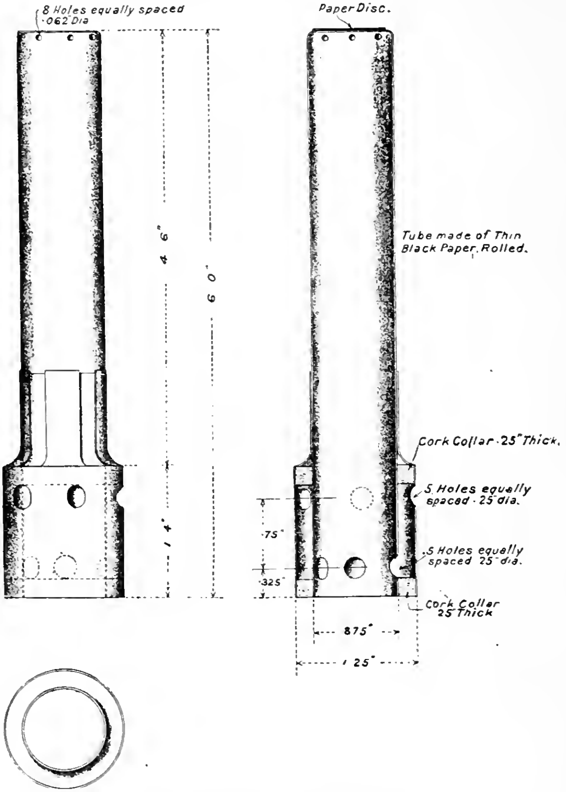


Fig. 147. Cap for Heat Test Tube
(From First Report of Heat Test Committee, by permission of the Controller of H.M. Stationery Office)

and materials used, and also to consider alternative tests. This Committee presented its first report in February, 1914, together with a Memorandum giving instructions as to the methods they recommended and specifications of all the apparatus and materials employed.[1] As light shining on the test-paper was found to shorten the test, a black cap (Fig. 147) was introduced. The tube is kept covered with this until shortly before the end of the test. The following Table shows briefly the temperatures, quantities and times for different sorts of explosives:

Explosive			Temperature of heat test bath	Quantity of explosive heat tested	Time explosive should stand the test
Class	Division	Name			
			°F.		min.
3	1	Nitro-glycerine extracted from dynamite, etc., by displacement with water . .	160 (71·1° C.)	2 c.c	15
		Carbonite, Monobel and similar friable nitro-glycerine preparations from which the nitro-glycerine cannot conveniently be extracted by water . .	160 (71·1° C.)	3·2 grammes	7
		Blasting Gelatine, Gelatine Dynamite and analogous preparations.	160 (71·1° C.)	3·2 ,, + 6·5 ,, French chalk	10
		Cordite,[1] Ballistite and other propellents of Class 3, Division 1	160 (71·1° C.)	1·6 grammes	10
3	2	Nitro-cellulose pulp, compressed Gun-cotton, Tonite and analogous compressed nitro-cellulose preparations .	170 (76·7° C.)	1·3 grammes	10
		Nitro-cellulose propellents	170 (76·7° C.)	1·3 ,,	10
		Ammonite, Bellite, Roburite and analogous preparations	170 (76·7° C.)	1·3 ,,	10

[1] For the acceptance of new Cordite and Cordite M.D. supplied for His Majesty's Naval and Military Services, the details are fixed by the Admiralty and War Office as follows:

		Cordite and Cordite M.D.	180 (82·2° C.)	1·6 grammes	30

Further investigations of the heat test have been interrupted by the war, except as regards the preparation of the iodide-starch papers.

United States Directions for the Heat Test

The regulations issued by the military and naval authorities of the United

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[1] *First Report of the Departmental Committee on the Heat Test as Applied to Explosives.* Wyman and Sons, 1914.

States differ considerably from the English ones. They are given in full. Blasting gelatine, gelatine dynamite, and analogous preparations are also submitted to liquefaction and exudation tests.

Nitro-glycerine. The water-bath of the potassium-iodide-starch testing-apparatus is brought to 160° F. (71·1°), and maintained at that temperature, being regulated by the thermometer which should be immersed about $2\frac{3}{4}$ inches in the water. The source of heat should be carefully watched, and at no time should the temperature of the bath rise or fall more than 1° F. from 160° F. Fifty grains of nitro-glycerine are placed in each test-tube and carefully weighed, care being taken not to get any on the sides of the test-tube: this may be done by using a suitable dropper or glass tube.

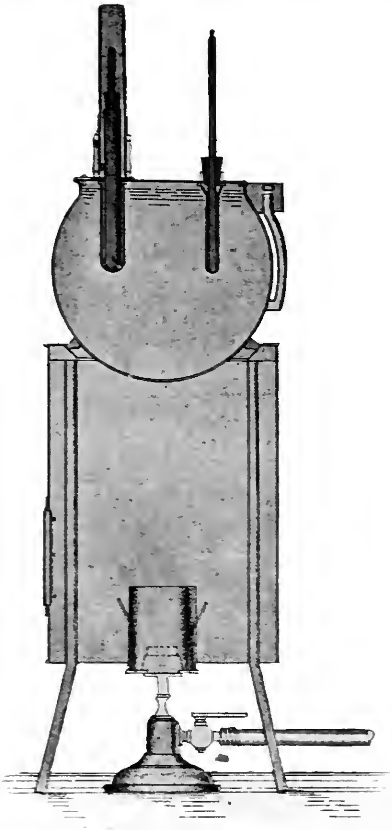

Fig. 148. Heat Test Bath Assembled (From First Report of Heat Test Committee, by permission of the Controller of H.M. Stationery Office)

A piece of test-paper is taken with the pincers and laid down on a piece of clean filter-paper. The test-paper is held in place by the end of a glass rod which has been thoroughly cleaned, heated, and cooled. A small hole is made in the test-paper with the point of the pincers opposite the middle of one end of the paper and about 0·2 inch from the edge. The test-paper is taken up with the pincers, the platinum hook inserted through the hole just made, the hook bent with the pincers until the throat of the hook is closed tightly on the paper so that it will stand stiffly up when the paper is held vertically above the glass rod. The glass rod with test-paper is placed carefully aside under a bell glass or other protecting cover where it will be protected from fumes and dust. In the same way the other test-papers are prepared.

A solution of pure glycerine and distilled water, in equal volumes, is prepared.

One of the test-papers is taken, held with the paper up, and a drop of the glycerine solution is placed on each of the lower corners of the test-paper, as held; the paper should absorb this evenly about half-way to the opposite upper edge, leaving a distinct line about midway between the moistened and the unmoistened parts. One of the test-tubes is placed in the bath through one of the apertures in the cover and is immersed until the sample is below the surface of the water. The test-paper, moistened with glycerine, is placed in the test-tube, and the glass rod is moved through the cork until the line between the moistened and unmoistened parts of the test-paper is about $\frac{5}{8}$ of an inch above the upper surface of the cover. This time is recorded. The same is done with each of the other two test-papers. The line between the moistened and unmoistened parts of each test-paper is watched carefully, and the exact instant that a faint brown colour [1] appears on this line of demarcation on each test-paper is recorded. This completes the test.

The nitro-glycerine under examination will not be considered "thoroughly purified" unless the time elapsed between the insertion of the test-paper and the appearance of the brown colour is at least fifteen minutes. The average of the records of all the tubes will be taken.

Explosive gelatine.

If explosive gelatine is under examination a sample of 50 grains is intimately incorporated with 100 grains of French chalk, using a wooden pestle in a wooden mortar. The French chalk should be of good commercial quality, should be thoroughly washed with distilled water, dried in a water-oven, and then exposed to moist air under a bell jar until it has taken up about 0·5 per cent. of moisture. It should then be placed in a glass-stoppered jar for use.

Each test-tube is filled with this mixture to a depth of $1\frac{3}{4}$ inches, the tube being gently tapped on a table to insure a proper degree of settling.

The heat test is then conducted as explained for nitro-glycerine. Explosive gelatine will not be considered as serviceable unless the average time of the test is at least ten minutes.

Gun-cotton.

The following are the tests for nitro-cotton as revised by the U.S. Ordnance Department, April 18, 1908:[2] The sample is pressed in a clean cloth or wrung in a wringer, if it contains a large excess of water. The cake is rubbed up in a cloth until it is a fine powder, taking care that it does not come in contact with the hands. It is spread out on clean paper trays, and dried in an air-

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[1] In order to detect this colour promptly, the water-bath should be so placed that a bright reflected light falls on the paper.

[2] Worden, *Nitrocellulose Industry*, p. 969.

bath at 35° to 42°, just sufficient time to reduce the moisture to that amount which will give a minimum heat test, this amount being from 1½ to 2 per cent. If, as sometimes happens in dry weather, the moisture has been reduced to less than 1·5 per cent., the sample must be placed in a moist atmosphere for a time not exceeding two hours, until the required moisture is obtained. The whole time of drying and making the test must not exceed eight hours.

The sample thus prepared is weighed out into five test tubes, 1·3 g. (20 grains) in each tube, so that a series is obtained covering the widest variation allowed for moisture. These tubes are 5·5 inches long, ½ inch internal diameter, and ⅝ inch external diameter, closed by a clean cork stopper fitting tightly, through which passes a tight glass rod with platinum holder for the paper. The corks are discarded after one test. The nitro-cellulose is pressed or shaken down in the tube until it occupies a space in the tube of 1⅝ inches. The test-paper, about 1 inch in length and 0·3 inch wide, is hung on the platinum holder, and moistened on its upper half with a 50 per cent. solution of pure glycerine in water. The heating bath, carefully regulated at 65·5° + 1°, is placed so that a bright reflected light is obtained, the tubes are placed in the bath and the time is noted. As the test proceeds, a slight film of moisture condenses on the inside of the tubes, and the line of demarcation between wet and dry test-paper is kept abreast of the lower edge of the moisture film. The first appearance of discoloration of the damp portion of the test-paper marks the end of the test for each separate tube, the minimum test of any one of the five tubes being the heat test of the nitro-cellulose. The standard water-bath is made long and narrow to reduce to a minimum the heating of the upper part of the tube.

Smokeless powder.

The sample should be prepared by cutting into slices 0·02 inch thick. These slices are exposed to the air for at least twelve hours.

The test-tube sample consists of 1·3 g.

The usual potassium iodide test is followed, except that the temperature is considerably higher for simple nitro-cellulose powders, being 100° (212° F.) instead of 65·5° (150° F.). Each sample must stand this temperature without showing a brown line for ten minutes.

Powders containing nitro-glycerine should stand the test at 65·5° for twenty minutes.

In France.

Nitro-cellulose is tested in France at 65° C. (169° F.) after the moisture has been brought to 1·3 per cent., which brings the test to the maximum of sensitiveness.[1]

Precautions

It is of the utmost importance that all the operations connected with the Abel and other trace tests be conducted in a room that is quite free from acid

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[1] Vennin et Chesneau, p. 244.

fumes, as the test is affected by very minute traces of acids and other bodies. If heat tests have to be carried out frequently it is best to keep a special room for the purpose or, better still, a special building remote from any place where acid or other fumes are generated. The operator also must be careful not to introduce anything that can affect the test: he should wash his hands before starting the test and should not wear clothes that can have become contaminated.

In 1901, Cullen called attention to the desirability of having a uniform official source for the heat test-papers used throughout the British Empire,[1] as very trifling differences in the method of preparation affect the results considerably. Heat test-papers can now be obtained from official sources.

The United States Government also issue heat test-papers to the manufacturers who contract to supply it with explosives.

If heat test papers from other than the official source be used, it is necessary to compare them with the official papers as regards sensitiveness by carrying out duplicate tests, or test them by the "diffusion test" described in the Memorandum on the Heat Test.

The objections to the test are due to its extreme sensitiveness. On the one hand, samples that are really stable sometimes give low heat tests, because they have become contaminated with minute traces of some material which is really harmless but affects the iodide and starch paper; ozone, for instance, has a powerful effect. On the other hand, samples of insufficient stability sometimes give high tests, because they contain traces of some substance that interferes with the reaction between the oxides of nitrogen and the paper. *Mercuric chloride* is a substance of this kind, for an extremely small proportion will lengthen the heat test of the sample very considerably. In Germany it has been usual to carry out the final washing of gun-cotton with water containing a little of this salt, ostensibly in order to prevent the growth of fungus on the gun-cotton; but this object can be better achieved by using phenol (carbolic acid), and it seems probable that the real object is to improve the heat test. At any rate, this is the view that has always been taken by the authorities in England, and they regard the addition of mercuric chloride or any similar masking agent as a most reprehensible practice. Tests for traces of mercury compounds are given elsewhere (p. 708).

There are many other substances, which mask the Abel heat test, and so make the explosives containing them appear much more stable than they really are. Ethyl acetate and alcohol prolong the test greatly, and consequently it cannot well be used to test powders gelatinized with them, at any rate, when they are new. Acetone, on the other hand, has little or no effect on the test. Dupré found that the carbonates of calcium and magnesium had no appreciable effect, whereas sodium carbonate prolonged the heat test

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[1] *J. Soc. Chem. Ind.*, 1901, vol. 20, p. 8.

of bad samples of explosives, with which it was mixed, but decreased that of good ones.[1] Camphor, aniline, diphenylamine, mineral jelly, and many other substances, which react with the oxides of nitrogen, prolong the heat test, but in many cases this prolongation corresponds to a real improvement in the stability.

In old explosives, the masking agents, if originally present, become exhausted, but varying quantities of a large number of decomposition products are present, which may affect the heat test, either lengthening or shortening it. Besides the organic compounds, water, nitric and nitrous acids are among the products, and as they are volatile, they may cause considerable fluctuations in the results, according as they are allowed to escape more or less before the test is applied. Oxalic acid shortens the heat test,[2] but probably does not affect the stability greatly.

Significance of heat test.

Robertson and Smart have carried out a number of experiments and calculations to ascertain the significance of the results of the Abel heat test in the case of nitro-glycerine and ungelatinized gun-cotton.[3] They found that the quantity of nitric peroxide required to produce the standard tint on the service heat test paper is 135×10^{-6} mg., a figure which is very near that arrived at in the laboratory of the Düneberg Explosives Factory, namely, 4×10^{-5} mg. nitrogen, equivalent to 131×10^{-6} mg. NO_2.[4] When the papers are exposed to an unlimited quantity of air containing nitric peroxide, the time required to produce the standard tint is inversely proportional to the concentration of nitric peroxide: for the service papers the product of the time in minutes by the concentration, in mg. of nitric peroxide per c.c., is 31×10^{-6}. From theoretical considerations Robertson and Smart deduced the equation:

$$T = \frac{KV}{Q} \log \frac{r}{r + \frac{Q^2}{KV^2} - \frac{QrT}{KV}}$$

where Q is the quantity of nitric peroxide required to produce the tint, 135×10^{-6}

K the product of the time into the concentration, 31×10^{-6}

V the unoccupied volume of the heat-test tube, 18 c.c.

r the rate of rise in the concentration of nitric peroxide in the heat test-tube due to decomposition of the explosive,

and T the time.

From the results obtained in the Will test and from other data it is calculated that for good gun-cotton $\log r = \cdot 06021\, t - 10 \cdot 6928$, where t is the temperature in °C. But there is a lag in the time of the test due to the fact that at first the gun-cotton is colder than the bath. The rate of rise of temperature

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[1] *A.R.*, 1887, p. 22.

[2] Bravetta and Parrozzani, *Stabilité des Nitro-celluloses*, 1908, p. 17.

[3] *J. Soc. Chem. Ind.*, 1910, p. 130.

[4] *Mitt. aus der Centralstelle*, Heft 3, p. 28.

was actually measured by means of a thermocouple. Taking into consideration the results thus obtained, the time for the heat test of gun-cotton was calculated for different temperatures and compared with those observed:

Temp. °C.	r	Time from equation	Lag	Calculated time	Observed time
		hr. min.	min.	min.	min.
70	0·332	27	4	31	28, 29
72	0·43	21·5	4	25·5	25, 25½
74	0·59	17	4	21	21, 21½
76·7	0·84	13	4	17	15
79·5	1·24	10	4	14	12
82·25	1·81	7·5	4	11·5	11½
100	21·26	1·75	4½	6·25	4½

The agreement, taken in conjunction with the results of other experiments, shows that in the case of fibrous gun-cotton the Abel heat test represents the decomposition of the gun-cotton itself during the test, and is not due to dissolved impurities. But with gelatinized smokeless powders, that have been made some time, this is not the case; the gun-cotton dissolves considerable quantities of nitrogen peroxide, which are not entirely given up again by the comparatively compact material, even when it is exposed to the atmosphere for some days in the ground state. It was found by A. C. Egerton that gun-cotton gave the same length of test when two papers were suspended in the test-tube instead of one.[1]

The reason why it is necessary to regulate the quantity of moisture in the gun-cotton is that, when very dry, it gives a high test owing to the drying of the test paper, whereas very wet gun-cotton also gives a high test, because the excess of water condenses in the tube and absorbs much of the nitric peroxide.

Since the heat test of a gun-cotton is only a measure of its initial decomposition, the test cannot be regarded as an absolute indication of its stability. In the Will test non-volatile catalysers may not give rise to a high rate of decomposition until fifteen or thirty minutes have elapsed at a temperature of 135° C., and this would correspond to a period of some days at 170° F. (76·7° C.).

When nitro-glycerine is heat tested in the ordinary way, the result obtained is very much higher than would be expected from the known rate of its decomposition, which is more than nine times as rapid as that of gun-cotton.

$$\log r = \cdot 06021\ t - 9{\cdot}7312.$$

This is due to the fact that the nitrogen peroxide formed mostly remains

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[1] *J. Soc. Chem. Ind.*, 1914, p. 113.

dissolved in the liquid, from which it can only escape slowly because but a very small surface is exposed. The result is largely dependent on the amount of oxide of nitrogen that has accumulated in the liquid. If a large surface be exposed by mixing the nitro-glycerine with silica wool, the results obtained agree with those calculated.

When small quantities of gun-cotton are added to nitro-glycerine, the heat test rises, owing either to the oxide of nitrogen being more soluble in the gun-cotton, or to the increased viscosity of the liquid. When sufficient gun-cotton has been added to break up the surface of the liquid, the heat test falls rapidly, but on account of the felting of the fibres the comminution is never so perfect as when silica wool is used. If the gun-cotton contains sulphuric ester, it greatly accelerates the decomposition of the nitro-glycerine and low heat tests are obtained. In the following experiments the gun-cotton A contained 0·15 per cent. of alkaline matter expressed as calcium carbonate, B was neutral, and C contained 0·7 per cent. sulphuric acid as sulphuric acid ester :

Per cent. N G	Per cent. G C	Temperature of test	Type of gun-cotton used		
			A	B	C
			min.	min.	min.
100	0	180°	19	14½	19
0	100	170°	17	17	16
97·5	2·5	180°	31	—	21
95	5	180°	32	15	30
90	10	180°	86	38	34
80	20	180°	28	13	9
70	30	180°	17	—	6
60	40	180°	13	6½	4

Other Trace Tests

Zinc iodide and starch test.

In Germany, the Netherlands, and some other countries a modification of the Abel test is used in which zinc iodide is substituted for potassium iodide, and it is claimed that the test is thereby rendered more sensitive. This, however, is hardly an advantage, as the principal fault of the Abel test is its excessive sensitiveness. In Spain a paper is used impregnated with a solution containing starch, zinc iodide, and zinc chloride.

Guttmann's test

Guttmann carried out a series of experiments to find a reagent which would not be masked by solvents such as ether-alcohol and ethyl-acetate, nor by such substances as mercuric chloride.[1] He decided upon a paper impregnated

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[1] *J. Soc. Chem. Ind.*, 1897, vol. 16, p. 293.

with diphenylamine in sulphuric acid solution. Of the diphenylamine 0·100 g. is dissolved in 40 c.c. of water together with 10 c.c. of concentrated sulphuric acid, and when cold an equal volume of pure glycerine is added. Filter-paper is well washed, dried, and cut into strips 1·0 inch by 0·4 inch. One of these strips is suspended from a hook, as in the Abel heat test, and the top edge is moistened with two drops of the reagent, so that they run together and cover about a quarter of the paper. Otherwise the test is carried out like the Abel test at a temperature of 70°. The moistened part of the paper after a time becomes greenish-yellow and then a dark blue mark appears at the dividing line between the moist and dry parts of the paper. This is the end of the test. The test has been adopted by the Belgian military engineers and is in use in several other countries, but unfavourable reports have been made by several investigators who have been unable to obtain concordant results with this test.[1]

Spica's test.

In Spica's test m-phenylene-diamine hydrochloride and cane-sugar are used to impregnate the paper. This reagent is much more sensitive than potassium iodide and starch, and for this reason has not been adopted extensively.

Several other "trace tests" have been proposed, but none of them has come into general use. J. Moir, for instance, has suggested the use of Ilosvay's reagent, mixed with glycerine, which is so sensitive that the test can be carried out at 45°; or a dilute solution of indole in 50 per cent. glycerine.[2]

Egerton proposes to do away with the paper and expose the reagent on a piece of glass in a tube of special design.[3] He also uses Ilosvay's reagent, which he prepares by mixing together 5 c.c. of a 0·1 per cent. solution of a-naphthylamine containing a little acetic acid, 5 c.c. of a 0·5 per cent. solution of sulphanilic acid also containing a little acetic acid, and 10 c.c. of glacial acetic acid.

Fume Tests

Vieille test.

In the Vieille test the explosive is heated in a closed tube with litmus-paper in a specially designed bath. The temperature of the bath is 110°, that of the sample 108·5°. The quantity of explosive taken is 10 g., preferably in one piece; this is heated in the bath for a day of eight hours or until the litmus-paper has assumed a standard red tint. Next day this is done again with a fresh piece of litmus-paper, and the procedure is repeated until the litmus-paper is reddened in one hour. All the times are then added together and the total time is noted. This test has been adopted officially in France and is also used considerably in other countries, but it is considered by some investigators to be unreliable.[4] Thus, in the Report on the *Iéna*

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[1] *See also* Kullgren, *S.S.*, 1912, p. 153.

[2] *Eighth Inter. Cong. Appl. Chem.*, 1912, vol. iv., p. 81.

[3] *J. Soc. Chem. Ind.*, 1913, p. 331; also *J. Soc. Chem. Ind.*, 1914, p. 113.

[4] *See* Sy, *Jour. Franklin Institute*, 1908, vol. 166, pp. 249, 321, 433.

Disaster [1] a case is mentioned in which duplicate tests on the same sample taken at different establishments gave results at twenty-two minutes and nineteen hours respectively, and at the same establishment duplicate tests often give very divergent results.[2] Sy ascribes the discrepancies to the difficulty in closing the tubes uniformly tightly.

Powders in naval service are considered dangerous when the test has fallen to fifteen hours, and in military service twelve hours.[3] More reliance is now placed in France on the examination of the stabilizer, diphenylamine.[4]

In Italy a modification of the Vieille test is used devised by Lepidi.[5] The powder is heated daily at 100° for ten hours and aerated for fourteen hours.

German 135° test.

The German test at 135° C. is much used for nitro-celluloses. The following are the particulars of the method as carried out in the United States Ordnance Laboratory.[6] 2·5 g. of the sample to be tested are dried at the ordinary temperature of the laboratory for twelve hours and placed in a strong test-tube. A piece of blue litmus paper is placed in the tube about ½ inch above the sample, the paper being folded lightly so as to give the folds sufficient elastic power to hold the paper in place by pressure against the sides of the tube. The tube is lightly closed by a cork with a hole 0·15 inch diameter bored through it, and so placed in a bath of boiling xylol (the boiling-point of which is 135°) that only 6 or 7 mm. project above the surface. Examination of each tube is made each five minutes after twenty minutes have elapsed. In making this examination the tube should be withdrawn only half its length and quickly replaced. Two tubes are used in each test, and there must be no failure in either tube. Three observations are made: (1) Time of *complete* reddening of litmus-paper: (2) time of appearance of brown nitric oxide fumes: (3) time at which the sample exploded.

Stable explosives should give the following times:

Explosive	Litmus not reddened in		No nitric fumes in		No explosion in
	hr.	min.	hr.	min.	hr.
Uncolloided nitro-cellulose . .	0	30	0	45	5
Nitro-cellulose powders . .	1	15	2	0	5
Nitro-glycerine powders . .	0	30	0	45	5

The results should be compared with that of a known stable explosive of the same kind, under the same test by the same operator, using the same

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[1] Vol. iii., p. 130.

[2] Vol. iii., pp. 177, 215.

[3] Buisson, *Problème des Poudres*, p. 215.

[4] Vennin et Chesneau, p. 423.

[5] E. Bravetta, *S.S.*, 1912, p. 496.

[6] *See* Sy, *J. Franklin Inst.*, as above, *also J. Amer. Chem. Soc.*, 1903, vol. 25, p. 550.

test-paper. Ungelatinized nitro-cellulose should be well shaken down in the tube by tapping, or lightly pressed down.

Waltham Abbey silvered vessel test.

The Waltham Abbey silvered vessel test is one which has been adopted by the War Office for the examination of Cordite Mark I, which has been in the Service for some time and gives a low heat test. It has been designed to imitate the conditions of storage as closely as possible, and is applied if the heat test at 160° F. is below eight minutes and above four minutes. Full instructions for carrying out the test are given in the *Regulations for Army Ordnance Services*, Part II (Wyman and Sons, 1908), pp. 162 to 167. The cordite is ground as for the heat test and about 50 g. are placed in a glass vessel surrounded with a vacuum jacket silvered to reduce loss of heat. To the neck of the vessel, and at right angles to it, is fused a long tube, which permits the

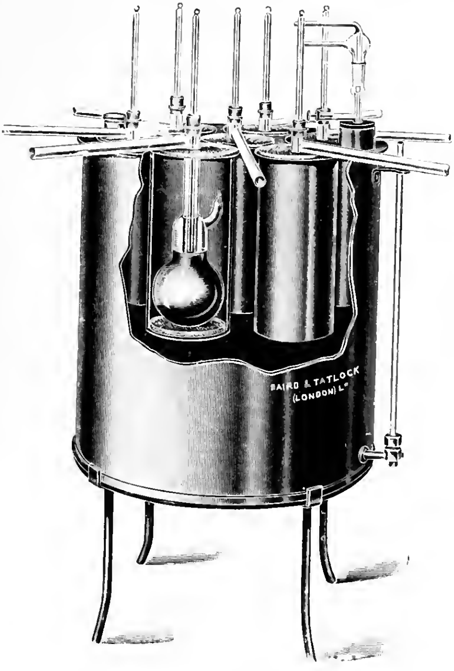

Fig. 149. Silvered Vessel Test

observation of any red fumes as soon as they are given off. A thermometer is introduced through the neck into the centre of the powder. These vessels are placed in recesses in the top of a bath, which is maintained at such a temperature that the thermometers indicate 80°. There is, however, no difficulty in keeping it constant within 0·1° if a Lowry gas regulator be used. After a time red fumes will appear in the side tube, and a few hours later the temperature of the cordite begins to rise. The time is noted when the temperature has risen 2·0°. A good cordite when new will stand this test for 500 or 600 hours. When the test has fallen below a certain limit the cordite is considered "unserviceable" and is destroyed. The test should be carried out in a special building in consequence of the danger of explosion of the considerable quantities of cordite involved. The temperature of the bath is kept constant by using a Lowry regulator if a gas supply be available; if not, the bath must be provided with a reflux condenser and filled with a liquid which boils at the right temperature; a mixture of water and methylated spirit is suitable.

Surveillance test.

In the United States a test has been adopted by the Joint Army and Navy Board in which 45 grammes of nitro cellulose powder are placed in a special stoppered bottle and placed in a magazine maintained at a temperature of 65·5° C. (150° F.), and the number of days is observed before red fumes appear. The time must not be less than 75 to 129 days according to the size of the grains, the larger the powder the greater the time. Whole grains of powder are taken and they are exposed to the air for twenty-four hours at 21° C. before the test. Samples often stand the test for several times as long as is required. The tests are carried out in triplicate.[1]

Fuming-off test.

The determination of the temperature at which a sample of explosive ignites or fumes off is not of great assistance as a rule in judging of its stability (*see* Chapter XXVIII). It is, however, of use in testing celluloid. A sample is cut into small pieces and 0·1 gramme is placed in a test-tube, which is immersed in an oil bath at 100°. The temperature of the bath is raised 5° a minute until the sample suddenly decomposes. The German Government has adopted this test for celluloid and has fixed the limit for satisfactory material at 150°.[2]

Quantitative Tests

Will test.

In the Will test, which is used as a rule only for ungelatinized nitro-cotton, the explosive is heated at a temperature of 135° in a current of dry carbon dioxide, and the nitrogen evolved is measured every quarter of an hour; 2·5 g. of the dry nitro-cotton are weighed out into the tube z, into which the

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[1] *See* Maj. E. P. O'Hern, *Smithsonian Report*, 1914, p. 257; *also* G. W. Patterson, *S.S.*, 1910, p. 48.

[2] W. Will, *Ang.*, 1906, p. 1377. *Report of Departmental Committee on Celluloid*, Cd. 7158, 1913, p. 16.

carbon dioxide passes through a spiral tube fused on to its lower end.[1] The rate of flow of the gas is rendered apparent by bubbling it through sulphuric acid, which at the same time dries it. Will generated the carbon dioxide in a Kipp's apparatus from marble and hydrochloric acid, using special precautions to free it from air, but Robertson preferred to take it from cylinders of the compressed gas carefully selected. It may also be generated from sulphuric acid and potassium bicarbonate solution. In any case the gas must be tested, and a correction introduced for the air it contains. From the tube z (Fig. 150) the gases pass to a copper tube U, containing metallic copper and copper oxide, which is maintained at a red heat. This destroys all organic gases, converting the carbon and hydrogen into carbon dioxide and water;

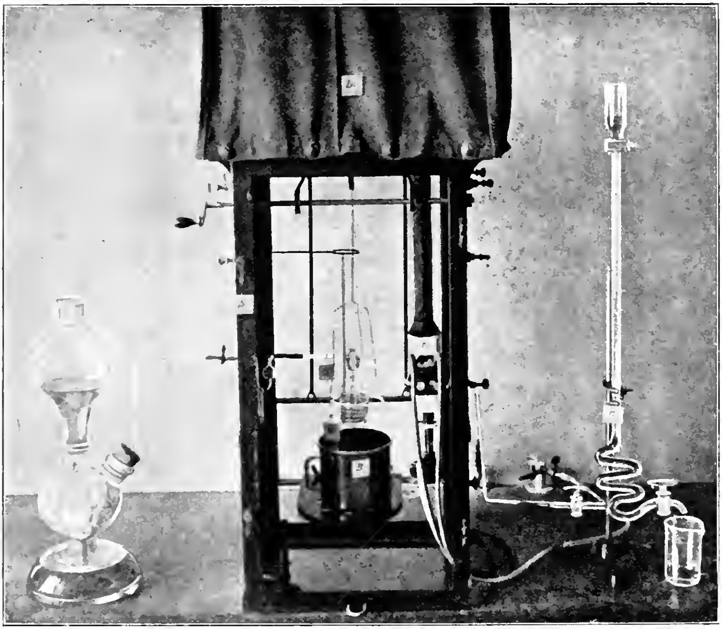

Fig. 150. Will's Test for the Stability of Nitro-cellulose

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[1] *See Mitteilungen aus der Centralstelle*, Heft 2, 1900; Heft 3, 1902; *also* Robertson, *J. Soc. Chem. Ind.*, 1902, p. 819.

nitrogen compounds are converted into elementary nitrogen. Hence the gases are led to the measuring tube *G*: this is filled with strong caustic soda solution of specific gravity 1·2: at its lower end there is a zig-zag to facilitate the absorption of the carbon dioxide. Carbon dioxide is passed through the apparatus until all air has been displaced, then the oil-bath *F*, which is kept at 135°, is raised and the test starts. There is a stirrer in the bath worked by a water-motor or other convenient means, and the whole is enclosed in the cupboard *S*, which keeps off draughts and protects the operator in the event of an explosion. Robertson has modified the apparatus in some details: he passes the gas at the rate of 1000 c.c. per hour instead of 1500, the rate used by Will, as he finds that the slower rate shows up bad gun-cottons more effectively.

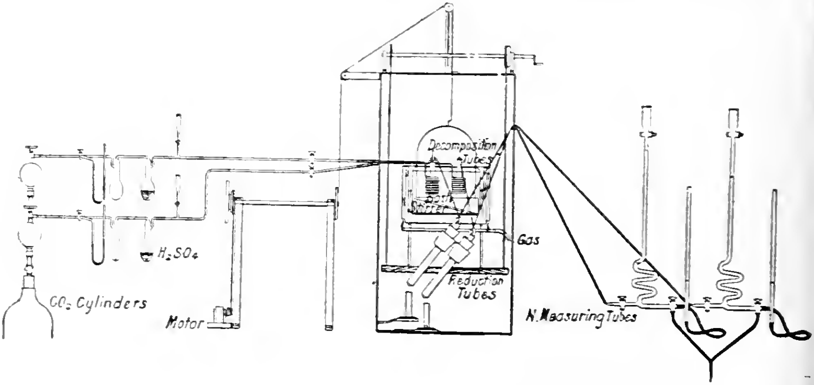

FIG. 151. Double Apparatus for Will Test. Robertson's Modification

The results given by the test are reliable, provided care be exercised to ensure that the apparatus is air-tight and working properly in all respects. A good gun-cotton evolves nitrogen at a uniform rate: for Service gun-cotton containing about 13 per cent. of nitrogen Robertson found that the quantity evolved in four hours by 2·5 g. was from 6·5 to 8·5 mg. Nitro-cottons less highly nitrated decompose less rapidly, provided they have been stabilized equally well. One reason why the Will test gives such uniform and satisfactory results is, no doubt, that air and moisture are excluded.

Robertson and Napper [1] have carried out experiments with a number of modifications of the test, and have thereby thrown considerable light on the composition of the gaseous products of decomposition, and their reciprocal influence on the decomposition.

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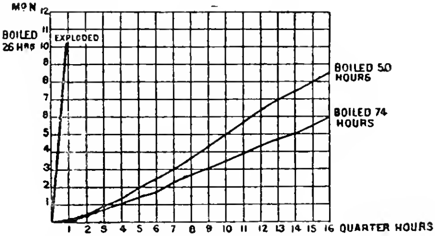
[1] *Trans. Chem. Soc.*, 1907, p. 761.

Bergmann and Junk test.

The Prussian military authorities and the German Railway Commission have adopted a test devised by Bergmann and Junk.[1] It has the merit of being quantitative and does not require such an elaborate apparatus as the Will test. In this test the gun-cotton is heated in a glass tube at 132°, and the nitrous gases are absorbed in water, and when the heating is finished they are estimated by the Schultze-Tiemann method. The glass tube has thick walls and is 35 cm. long and 2 cm. in internal diameter. Into the neck is ground a hollow glass stopper, which is surmounted by the absorption apparatus shown, *D* or *E*, Fig. 153.

The heating bath is a rectangular copper vessel 35 cm. × 10 cm. × 25 cm. high, with ten tubes, each 20 cm. long, let into it to take the glass tubes. It is also fitted with a reflux condenser and a small tube to take a thermometer; it is filled with amyl-alcohol, which is kept boiling by means of a burner.



Service gun-cotton. Influence of boiling

FIG. 152. Results of Will Tests

In the authors' paper there is a description of an elaborate wooden cupboard to take the testing apparatus, so that in case of an explosion the effects may be confined. It is, however, expensive and greatly increases the danger of fire. A large piece of plate glass should be erected in front of the apparatus with a piece of woven wire before it, and there should be an arrangement of cords and pulleys to enable the operator to remove any tube from the bath without handling it.

The gun-cotton is dried in a bath with a good current of air at a temperature of 40° to 50° for three hours. Then it is passed through a sieve of 2 mm. mesh, and the drying is continued in a vacuum desiccator over sulphuric acid until it contains not more than 1 per cent. of water; 2 g. are weighed out and introduced into the tube, any particles adhering to the sides being removed by knocking the tube or brushing it down with a feather. The glass stopper is slightly lubricated with good mineral lubricating oil and is inserted, the absorption apparatus is half-filled with water, and the glass tube is introduced into one of the holes in the bath, which should be at a temperature of 132°. The heating is continued for two hours or other convenient time, and then the tube is removed from the bath. As the air in the tube contracts the water is drawn out of the beaker *g* on to the cotton. If the bulb apparatus *E* be used, it is necessary to add some water at the end of the test to cause it to siphon over into the tube. The absorption apparatus is washed out into the

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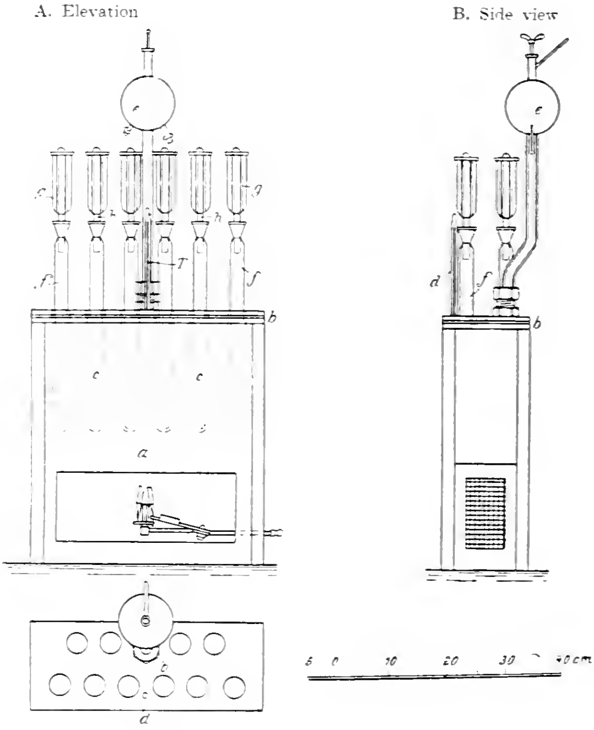
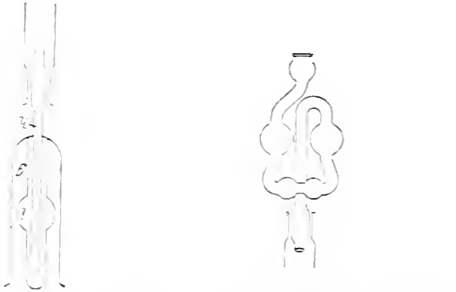
[1] *Ang.*, 1904, p. 982.



C. Plan



D. Beaker absorption apparatus E. Bulb absorption apparatus

FIG. 153. Bergmann and Junk Stability Test for Nitro-cellulose

tube, and the volume is made up to the 50 c.c. mark, which is on the tube. The liquid is then filtered through a dry filter, 25 c.c. of the filtrate are taken, 1 c.c. of N/2 potassium permanganate solution is added to oxidize the nitrous to nitric acid, and the nitrogen is estimated by the Schultze-Tiemann method. A good gun-cotton in two hours should not give more than 2·5 c.c. of nitric oxide and a collodion cotton not more than 2·0 c.c. Dupré came to the following conclusion concerning the test : [1]

"It was found, in the first place, that duplicate experiments with the same sample of gun-cotton gave as a rule very concordant results, but that, in the second place, the test was influenced to a considerable degree by variation in the percentage of moisture in the samples tested. This was more especially found to be the case when the sample was not perfectly purified, and might thus easily lead to mistaken decisions with regard to the rejection or approval of samples near the limit of purity, unless certain limits of moisture are very rigidly observed.

"The test is scarcely influenced at all by the presence of perchloride of mercury, which, as is well known, renders our heat test inapplicable, but like this latter test it is greatly influenced by the presence of urea. The test is also greatly affected by the condition of the gun-cotton tested, *i.e.* whether gelatinized or simply pulped, the former giving far lower results than the latter. The test in its present form is not applicable to nitro-glycerine preparations or to such as contain nitrates, and does not distinguish so sharply as the heat test between the various stages of washing of gun-cotton. Lastly, in spite of all care taken, tests made on the same sample gave occasionally widely different results, due perhaps to the fact that the products of decomposition are left in contact with the sample throughout the test, whereby very small differences in the rate of decomposition at the beginning of the experiment would be greatly aggravated at the end."

Sy's test.

In this test, which is known also as the "U.S. Army Ordnance 115° C. test," whole pieces of nitro-cellulose powder are weighed out on watch glasses and then placed in a bath at 115° for eight hours. The sample is reweighed and the heating is repeated for a further eight hours next day, and so on for six days.[2] The loss of weight must not exceed that permitted for powder of that particular web thickness :

Web thickness	Loss
·020 inch	6·8 per cent.
·060 ,,	7·45 ,,
·100 ,,	8·1 ,,
·140 ,,	8·5 ,,

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[1] *A.R.*, 1904, p. 28. *See also A.R.*, 1905, p. 28.

[2] See A. P. Sy, *J. Amer. Chem. Soc.*, 1903, p. 161 ; *J. Frank. Inst.*, 1903, p. 161, E. M. Weaver, *Military Explosives*, 3rd Ed., p. 186.

The temperature of the bath should not vary more than ½° from 115°; it may be maintained by filling the space between the walls of the oven with a mixture of toluene and xylene and boiling it under an inverted condenser.

Other quantitative tests.

Various investigators have devised tests in which the gun-cotton is heated *in vacuo* to a temperature of 130° to 150°, and the evolution of gas is measured, generally by means of a manometer. Obermüller described a test of this kind,[1] and Willcox has given the results of determinations with it on American gun-cottons: [2] Pleus has given details of apparatus for carrying it out.[3] Dupré has used a similar method and reported favourably on it.[4] Brame also has devised a test of this sort.[5] Robertson and Napper have pointed out the necessity of preventing moisture depositing in the tubes leading away from the decomposition vessel.[6] The method gives results as satisfactory as those of the Will test, if proper precautions be taken.

Mittasch heated gun-cotton at the ordinary pressure at 150° and recorded the increase of volume automatically.[7] Silberrad devised a similar test, in which the gun-cotton was dried and then heated at 115° for twenty hours, and the gas evolved was measured over water.[8] Dupré found that duplicate tests with the same sample conducted side by side occasionally gave widely different results.[9]

Silberrad [10] has also proposed a test for smokeless powders, in which the unground powder is heated at a temperature of 70° in a limited quantity of air, and the rate and duration of the gas evolution, or contraction due to absorption of the oxygen, is observed. The results do not seem to bear any relationship to the real stability of the powder.

Calorimetric test.

As a measure of the deterioration of an explosive the diminution of its calorific power can be taken.[11] This is determined before and after storage at a more or less elevated temperature by simply exploding some in a calorimetric bomb with the usual precautions.

Light Tests

Abel in his classical Researches on Gun-cotton [12] investigated the action of sunlight on this explosive. He found that it became acid and evolved gases

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[1] *Berlin Bezirksverein der Verein deutscher Chemiker*, October 11, 1904; *J. Soc. Chem. Ind.*, 1905, p. 347.

[2] *J. Amer. Chem. Soc.*, vol. 30, p. 271; *S.S.*, 1908, p. 247.

[3] *S.S.*, 1910, p. 121.

[4] *A.R.*, 1903, p. 26; 1904, p. 28; 1905, p. 29.

[5] *J. Soc. Chem. Ind.*, 1912, p. 161.

[6] *Trans. Chem. Soc.*, 1907, p. 764.

[7] *Ang.*, 1903, p. 929; *see also* Saposhnikof, *P. et S.*, vol. 14, p. 42.

[8] *Treatise on Service Explosives*, 1907, p. 141.

[9] *A.R.*, 1905, p. 28.

[10] *Ibid.*

[11] E. Berger, *Bul. Soc. Chim.* (4), 11, p. 1, 1912.

[12] *Phil. Trans.*, 1867, 181.

much more rapidly than in the dark. When thoroughly stabilized the decomposition was less rapid than when part of the stabilization process was omitted. If the gun-cotton was wet, the decomposition was considerably greater than if it was air-dry, which is the reverse of what is found when the gun-cotton is stored in the dark. Abel ascribed this phenomenon to oxidation of the gun-cotton at the expense of the water under the influence of the light. It took months or years to obtain a marked evolution of gas from a stable gun-cotton; for this reason, and because of the variability of sunlight, but few attempts have been made to investigate the stability of explosives by insolation. Berthelot and Gaudechon have carried out a number of experiments, in which various explosives have been enclosed in quartz tubes and exposed to ultra-violet light from a mercury lamp.[1] They find that the gas evolved from Poudre B in good condition consists of carbon monoxide and dioxide and nitrogen, whereas from deteriorated powder nitrous and nitric oxides are also given off. Nitro-glycerine and nitro-glycerine powders give off the oxides of nitrogen even when new, and hence the authors conclude that nitro-cellulose powders have a greater intrinsic stability than those that contain nitro-glycerine. A test which submits an explosive to conditions fundamentally different from those it will have to undergo in actual use, cannot, however, fairly be used to compare substances of different types, though possibly it may afford evidence of the comparative stability of explosives of the same sort. The results given by this test have, however, been found to be too discordant to be of practical use.[2]

Examination of Stabilizer

Although many of the above tests give fairly satisfactory results when used for the examination of freshly manufactured explosives, great difficulties are encountered when they are applied to old explosives, such as smokeless powders which have been stored in a hot climate for some years. The products of deterioration accumulated in the powders affect the results, and at high temperatures they may bring about decomposition of quite a different kind from that which occurs at the ordinary temperature of storage. On the other hand, it is often practically impossible to prevent the escape of a considerable proportion of the volatile products of decomposition during the preparation of the sample and the course of the test. If a stabilizing agent was originally added to the explosive, useful information can often be obtained by examining it. In the case of compressed gun-cotton, for instance, into which a small proportion of calcium carbonate was incorporated during manufacture, the course of the deterioration can be ascertained by determining how much of it has been converted into nitrite and nitrate, and how much is still unchanged.

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[1] *Compt. rend.*, 1911, p. 1220; 1912, pp. 201 and 514.

[2] Vennin et Chesneau, p. 416.

And from the results the probable future life of the gun-cotton can be calculated.

Diphenylamine.

If the explosive contain diphenylamine it will on storage become blue, and the colour will gradually darken until it becomes practically black. This discoloration is not to be taken as an indication that the life of the powder is drawing to a close, for it appears comparatively early. The gradual exhaustion of the stabilizer can, however, be followed readily by extracting it from the powder and applying certain reactions.[1] The decomposition of the nitrocellulose and the consequent liberation of oxides of nitrogen converts the diphenylamine first into diphenyl-nitrosamine, then into nitro-diphenyl-nitrosamine, dinitro-diphenylamine and finally trinitro-diphenylamine.[2] The nitration of the stabilizer does not proceed beyond the trinitro-derivative, and the presence of this compound indicates that the life of the powder is nearing its close.

$(C_6H_5)_2NH$	diphenylamine
$(C_6H_5)_2N.NO$	diphenyl-nitrosamine
$C_6H_4(NO_2).N(NO).C_6H_5$	nitro-diphenyl-nitrosamine
$(C_6H_4NO_2)_2NH$	dinitro-diphenylamine
$C_6H_4(NO_2).N.C_6H_3(NO_2)_2$	trinitro-diphenylamine

To test for these different compounds 10 grammes of finely divided powder are digested for twenty-four hours with 100 c.c. of alcohol. To test for diphenyl-nitrosamine 5 c.c. of the solution are boiled with 1 c.c. of a 5 per cent. solution of α-naphthylamine. The nitrosamine gives a fine red colour. The quantity of it present can be estimated approximately by comparing the colour with that given by known quantities of nitrosamine, but in this case the powder must be extracted for several days with successive quantities of alcohol, and a larger quantity of solution must be taken.

The dinitro-diphenylamines are detected by adding a few drops of alcoholic potash or soda to 5 c.c. of the alcoholic extract. They give a red coloration, as also do the trinitro-diphenylamines. But the latter can be detected by the red coloration they give when a few drops of a saturated alcoholic solution of potassium cyanide are added to 5 c.c. of the alcoholic extract.

The quantity of unchanged diphenylamine, together with the diphenyl-nitrosamine, can be determined by digesting the powder with soda, distilling with steam and titrating with bromine. The details of the method are given in Part XII under the heading "Diphenylamine." This gives a measure of the amount of stabilizer still available in the explosive, for the nitrosamine is an efficient stabilizer also. The quantity of nitrosamine is at a maximum when from a half to two-thirds of the life of the powder has elapsed.[3]

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[1] See Buisson, *Problème des Poudres*, p. 126.

[2] *See also* P. Juillard, *Bull. Soc. Chim.*, 33, 1905, p. 1172.

[3] E. Berger, *loc. cit.*

PART XII

MATERIALS AND THEIR ANALYSIS

MATERIALS AND THEIR ANALYSIS

Sampling : Moisture : Ether extract : Aqueous extract : Specific gravity separation : Residue : Literature : Acetone : Acids, sulphuric, nitric, mixed, waste acid : Alcohol, ethyl : Ammonium oxalate : Antimony sulphide : Azides : Chlorate of potassium : Chlorhydrin, dichlorhydrin, chlor-dinitrohydrin : Cotton, absorption of dye, copper value, hydrate copper value, wood-gum, viscosity, acid value, determination, dead fibres, unripe fibres, specifications : Diphenylamine : Ether : Fulminate of mercury, manufacture, properties, estimation : Fulminate of silver : Fulminating mercury and silver : Glycerine : Glycerine nitrates (lower), dinitroglycerine, mononitro-glycerine : Graphite : Hexanitro-ethane : Kieselguhr : Mercury, detection of traces by spectroscopic methods, microscopic methods : Mineral jelly : Moisture : Nitrates, ammonium nitrate, potassium nitrate, sodium nitrate : Nitro-cellulose, properties, nitrogen, detection, estimation, determination of nitrogen, solubility, matter insoluble in acetone, unnitrated fibre, free acid and alkali, discoloration, ash, microscopic examination, sulphuric esters, viscosity of solutions, fineness : Nitro-compounds, melting-point, colour reactions, impurities, nitrogen determination, Kjeldahl method, decomposition flask method, stannous chloride method, titanium chloride method : Nitroglycerine, properties, physiological action, detection, examination, estimation : Tretanitro-diglycerine : Parchment paper : Picric acid, properties, detection, estimation, examination, density : Picrates and trinitro-cresylates, ammonium picrate : Sulphur : Tetranitro-methane : Wood-meal

The analysis of an explosive often presents special difficulties. Details of the methods used are given under the heads of the various substances, but are preceded by some general remarks.

Sampling. If the explosive be in the form of powder or small grains, portions should be taken from different parts of the bulk and thoroughly mixed together. The size of the sample can then be reduced by quartation. The powder is poured out so as to form a conical heap, and this is then divided in half by means of a spatula passed down through the apex of the cone. One of the halves is then divided again into half in the same way. One of the quarters is then removed and can, if necessary, be again divided into quarters by pouring again and dividing in the same way. If the explosive be in the form of sticks, some of them should be selected from various parts. It is often well to cut off and discard the ends of the sticks. The sticks may then be cut into small pieces and mixed, and a portion of the sample may then be ground and mixed again. If the explosive be in paraffined wrappers, care should be taken not to get any flakes of paraffin mixed with it. Some explosives tend to segregate some of their constituents on standing in a bottle. This is notably the case with mixtures containing much nitro-glycerine and only a small proportion of absorbent. Such samples should be remixed just before taking a portion for analysis.

Moisture. A determination must, of course, be made of the percentage of moisture in the sample. If the explosive contain nitro-glycerine or other volatile substance special precautions must be taken.

Ether extract If the explosive contain organic substances it is generally advisable to extract it first with ether, which dissolves out nitro-glycerine and similar substances, nitro-aromatic compounds, sulphur, fats and oils, and resins. It is best to use pure ether (not methylated) as it extracts less from wood meal or nitro-cellulose, if present. If the explosive contain much moisture, it should be dried first partially by standing in a desiccator over sulphuric acid for twenty-four hours. The extraction can generally be carried out in a beaker in which the sample is treated with successive portions of the solvent, but smokeless powders should be extracted in a Soxhlet. The nitro-glycerine is estimated from a determination of the nitric groups in the ether-soluble portion. The estimation of nitro-aromatic compounds is difficult if there be more than one of them present, or if the explosive also contain oil or fat, for these substances are all soluble more or less in organic solvents. The nitrogen in them can be estimated, and various qualitative tests can be applied, and usually it is possible to isolate a little of the pure substance and determine its melting point. Nitro-glycerine can be separated from sulphur, mineral jelly and various other substances by extracting with 80 per cent. methyl alcohol or 70 per cent. acetic acid at the ordinary temperature. Resin can be estimated by saponifying with alcoholic alkali, diluting with water, extracting with ether, and acidifying the aqueous liquid. The resin is thus reprecipitated and can be determined by extracting with ether, evaporating down and weighing, or by again saponifying with a known quantity of alkali and titrating back the excess.

Aqueous extract. The residue from the ether extraction is next extracted with water. If the explosive contain flour or starch, the water should be cold, as hot water would gelatinize it. Cold water should also be used for samples containing wood meal, as this gives up some of its constituents to hot water. The water extract contains the inorganic nitrates, chlorates, perchlorates and chlorides, ammonium oxalate and any other soluble salts, also glycerine and aniline chloride if present, and part of the dextrin, gum, starch and gelatine, the amount depending on the coagulating power of the salts. In the presence of starch Snelling and Storm recommend the use of a porous alundum filter for filtering off the aqueous extract. Gum arabic, which is sometimes added as a binding agent, may be detected by the precipitate it gives with basic lead acetate.

Specific gravity separation In some cases chemical analysis fails to distinguish between two or more possible mixtures of salts having the same ultimate composition. It is, for instance, impossible from the results of chemical analysis to distinguish a mixture of ammonium nitrate and sodium chloride in equivalent proportions from one of sodium nitrate and ammonium chloride. In such cases Storm and Hyde [1] separate the salts by the use of a liquid in which one or more of the salts floats whilst others sink. Mixtures of bromoform (specific gravity 2·83) and chloroform (specific gravity 1·49) are suitable for this purpose. The explosive is first extracted with ether to remove nitro-glycerine, oils and other materials, which tend to cause the particles to cling together. The residue is then dried in an oven and ground rapidly. About 10 grammes are mixed with 25 c.c. of a suitable mixture of bromoform and chloroform and introduced into a separating funnel having a cock with an extra wide bore. More liquid is then added, it is stirred with a glass rod and allowed to stand for a time. The heavy salt that collects at the bottom is then drawn off rapidly, the liquid is decanted off and the crystals are examined chemically. The lighter salts together with wood meal, etc., floats on the surface of the liquid in the funnel. These can be further separated by the use of a lighter liquid mixture. The separation is never complete, because the particles of the different substances tend to cling together, especially if they are not quite dry, but a qualitative analysis of the materials separated will usually suffice to show what are the salts present. The following are the specific gravities of the inorganic substances most likely to be present :

Substance	Specific gravity
Ammonium nitrate	1·72
,, chloride	1·52
,, sulphate	1·77
,, alum (crystals)	1·62
,, perchlorate	1·87
,, oxalate + H_2O	1·50
Sodium nitrate	2·26
,, chloride	2·17
,, sulphate + $10H_2O$	1·46
,, ,, (anhydrous)	2·66
Potassium nitrate	2·09
,, chloride	1·99
,, alum (crystals)	1·75
,, sulphate	2·66
,, chlorate	2·33
,, perchlorate	2·52
Magnesium sulphate + $7H_2O$	1·68
,, ,, (anhydrous)	2·65
,, carbonate	3·04
Calcium carbonate (precipitated)	2·72
,, sulphate + $2H_2O$	2·32
,, ,, (anhydrous)	2·97
Barium nitrate	3·23
Manganese dioxide	5·03

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[1] C. G. Storm and A. L. Hyde, *U.S. Bureau of Mines, Technical Paper* 78.

Residue. The residue insoluble in water may contain nitro-cellulose, calcium carbonate, calcium oxalate, kieselguhr, talc, wood meal, flour, tan meal, curcuma, metallic aluminium, etc., also small quantities of such substances as graphite, soot or a dye. Treatment with dilute acid will dissolve the carbonate and oxalates and the starchy materials, as also metals. By examination under the microscope the remaining substance or substances can be identified. Dextrin, gums and gelatine are generally determined by difference, but they give qualitative reactions which enable them to be identified in most cases. Starch may be recognized by the fact that it dissolves in boiling water, and is coloured blue by iodine. Nitro-starch is not coloured by iodine. Wood meal gives a characteristic colour with phloroglucinol reagent. For microphotos of some of the materials that may be present, see *U.S. Bureau of Mines Bulletin*, No. 96, pp. 94, 96, 98.

Calcium silicide may be recognized by the fact that it dissolves in dilute hydrochloric acid, giving off hydrogen and silicon hydride, which is spontaneously inflammable.

Literature. "Analysis of Black Powder and Dynamite," by W. O. Snelling and C. G. Storm. *U.S. Bureau of Mines Bulletin*, No. 51.

"Analysis of Permissible Explosives," by C. G. Storm, *U.S. Bureau of Mines Bulletin*, No. 96.

Article by E. Küppers, "Glückauf," No. 41, 1914; *S.S.*, 1915, p. 145.

ACETONE

$CH_3.CO.CH_3$. Molecular weight 58·06

(*See also* Chapter XXIV)

Acetone is a mobile colourless liquid having a specific gravity 0·7971 at 15° compared with water at 4°, and boiling at 56·1° under a pressure of 760 mm. The solvent used for the manufacture of smokeless powder should have a specific gravity of not more than 0·800 at 15° compared with water at the same temperature. It should be colourless and miscible with water in all proportions without turbidity, and should leave practically no residue on evaporation.

Permanganate Test. A 100 c.c. graduated flask is filled up to the mark with the acetone at a temperature of 15°, and 1 c.c. of a 0·1 per cent. solution of potassium permanganate is added, and the two are mixed. The characteristic colour of the permanganate should persist for at least thirty minutes. This test is affected by light, and should be carried out in the dark or in a dim light. It excludes various organic impurities.

The deterioration of acetone is greatly accelerated if it contain acids or certain amines. These are tested for by diluting with an equal volume of distilled water and adding a few drops of a saturated solution of para-nitrophenol or other suitable indicator. The acetone should be quite neutral to this

Acetone

indicator, or only show very slight alkalinity. No acid should be present except carbonic, which is determined by diluting with boiled distilled water and titrating with standard caustic alkali, using phenolphthalein as indicator. The amount of carbon dioxide should not exceed 0·002 per cent.

In Germany acetone is tested for neutrality with phenolphthalein which, when added to 10 c.c. of the acetone, must not be reddened, but the addition of 1 c.c. N/10 alkali must cause a red coloration. It is also specified that it shall not contain more than 0·1 per cent. of "aldehyde," which is tested for with a solution made by dissolving 3 g. silver nitrate, 3 g. caustic soda, and 20 g. liquid ammonia (specific gravity 0·9) in water and making up to 100 c.c.: 10 c.c. of the acetone are mixed with 10 c.c. distilled water and 2 c.c. of the silver solution, and left covered in the dark for a quarter of an hour. The liquid is then poured off from the reduced silver, and tested with a dilute solution of ammonium nitrate to see whether excess of silver be still present. If there be, it is supposed that the amount of aldehyde in the acetone is less than 0·1 per cent. Although acetones occasionally fail to pass this test, it is doubtful whether the failure is ever due to aldehyde, the quantity of which seldom exceeds 0·01 per cent. There is no method of determining accurately small quantities of aldehyde in the presence of large quantities of acetone, but they can be estimated approximately by colorimetric tests with Schiff's reagent, a solution of magenta decolorized with sulphurous acid. If 2 c.c. of acetone be dissolved in 100 c.c. of water and 1 c.c. of the reagent be added, the liquid gradually assumes a purple colour, which is distinctly stronger if 0·01 per cent. of aldehyde has previously been added to the acetone.

The test with ammoniacal silver nitrate solution is really a test for the light oils which are present in acetone and are insoluble in water. These can be determined by actual measurement as follows: 100 c.c. of acetone are mixed with 200 c.c. of water in a retort, and rapidly distilled. The first 10 c.c. of distillate is collected in a graduated cylinder, 20 c.c. of water are added, and if the liquid becomes cloudy, the cylinder is stoppered and allowed to stand. The volume of oil that separates at the top of the liquid is then read off, if there be sufficient to give a reading. A cloudiness of the liquid in the clylinder indicates that the quantity of the impurity in the acetone is not less than 0·02 per cent.

A more convenient test for the same impurity is carried out with N/10 iodine solution (12·69 g. iodine and 14·60 g. potassium iodide dissolved in 1 litre water): 100 c.c. of water at a temperature of 15° are placed in a beaker, 10 c.c. of the acetone are then run in and mixed with the water, and then 2 c.c. of the iodine solution. Exactly one minute later the same quantity of N/10 thiosulphate solution is run in, and the excess is then titrated with N/100 iodine solution; 1 c.c. of this is equivalent to about 0·02 per cent. of the impurity. If the quantity required be more than 10 c.c., the test should be repeated, using larger quantities of N/10 iodine and thiosulphate. Provided there be a sufficient excess of iodine, the results are not affected by the quantity of it added. They are also not affected by light, and only slightly by variations in the proportion of water and acetone used, or by small differences in the time of action, or by such quantities of alkaline bodies as are liable to be present in a good acetone. The temperature should be regulated carefully.

For the detection of acetone see, Allen's *Commercial Organic Analysis*, 4th edition, vol. i., p. 105.

Acetone can be estimated by Messinger's method: 2 g. of acetone are weighed out and dissolved in 500 c.c. water; of this solution 10 c.c. are measured out, mixed with 25 c.c. N/1 alkali, and 50 c.c. N/10 iodine solution are added. The liquid is shaken frequently for fifteen or twenty minutes, then 26 c.c. of N/1 sulphuric acid are added, and the iodine is titrated with N/10 thiosulphate solution. The test depends upon the conversion of the acetone into iodoform, whereby 6 atoms of iodine are absorbed for each molecule of acetone. In Germany it is required that the acetone shall show at least 98 per cent. by this test.

Acetone can also be estimated by the method of Jolles,[1] which depends upon the fact that a molecule of acetone combines with a molecule of sodium bisulphite to form a compound, which no longer reacts with iodine in neutral solution. The standard bisulphite solution is added to the acetone solution in a quantity three or four times as great as the theoretical amount, and the excess is titrated with standard iodine solution, after the mixture has been allowed to stand for not less than thirty hours. A blank determination should be made simultaneously.

In mixtures of acetone and water containing not more than 25 per cent. acetone the percentage can be calculated from the specific gravity using the formula $w = 360\,(d - 0{\cdot}8)$, where w is the percentage of water and d the specific gravity of the liquid.

ACIDS

Sulphuric Acid. H_2SO_4, molecular weight 98·03 (*see also* Chapter VII). The specific gravity is usually determined, but in the case of C.O.V. gives but little indication of the exact strength, which is generally ascertained by titration. It may, however, be estimated by diluting to about 75 per cent. strength with a known proportion of water and determining the specific gravity.[2] The mineral matter is determined by evaporating in a platinum basin and igniting (*see also* Chapter VII): it should not exceed 0·1 per cent. Arsenic is determined by diluting with water and passing sulphuretted hydrogen. The precipitated sulphide of arsenic can be determined gravimetrically or

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[1] *Ber.*, 1906, p. 1306.

[2] A. Marshall, *J. Soc. Chem. Ind.*, 1902, p. 1511.

Acids

volumetrically. The acid should not give more than 0·01 per cent. As_2S_3. Iron is almost insoluble in the concentrated acid, but may be present in diluter acid or in oleum. It is objectionable, if the acid is to be used for the manufacture of picric acid. According to a French Government specification before the war, C.O.V. for the manufacture of nitro-cellulose must have a density of 65·5° B., corresponding to a density of 1·831, and must not contain more than 0·05 per cent. residue or 0·03 per cent. iron. Oleum must not contain more than 0·07 per cent. residue or 0·04 per cent. iron.[1]

Nitric Acid. HNO_3, molecular weight 63·02 (*see also* Chapter VIII). The specific gravity in this case affords a measure of the strength, when corrected for nitrous acid (*see* Chapter VIII), which is determined by dissolving 5 g. in a litre of water and titrating with N/10 permanganate solution until the colour remains for at least fifteen minutes; 1 c.c. is equivalent to 0·00235 g. HNO_2. The residue is determined by evaporation on a water-bath, and is tested for sulphuric acid. The nitric acid is also tested for chlorides by diluting and adding silver nitrate solution. It should not give more than 0·1 per cent. residue or 0·1 per cent. AgCl.

Mixed Acid. The total acidity is determined by titration, the nitric and nitrous acids are estimated together by means of the nitrometer, and the nitrous acid by titration with permanganate. The percentages of nitric and sulphuric acid are then obtained by subtraction. The sum of the nitric and nitrous acids can also be estimated by precipitation with nitron. Direct determination of the sulphuric acid by evaporating off the nitric acid on a water-bath and subsequent titration gives low results; precipitation with barium chloride is also unreliable.[2]

Waste Acid from the nitration of cellulose can be analysed by the same methods. That from the manufacture of nitro-glycerine presents difficulties, because a few per cent. of nitro glycerine dissolve in the acid with partial decomposition. In the nitrometer the nitro glycerine gives off the whole of its nitrogen; it is better therefore to use nitron.

G. Finch[3] determines the total acidity of mixed and waste acids by titrating with barium hydroxide solution in the presence of phenol-phthalein. The barium sulphate is then filtered off and titrated with a standard neutral solution of potassium chromate free from carbonic acid until the liquid is faintly yellow. This gives the quantity of barium nitrate and nitrite and therefore the amount of nitric and nitrous acids. The results are not affected by the presence of nitro-glycerine and other organic matter in the acid.

Revivification of Waste Acids. During the nitration process the main reaction results in the consumption of a certain quantity of nitric acid and the formation of the equivalent quantity of water. In the manufacture of nitro-

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[3] Buisson, *Problème des Poudres*, p. 22.

[2] Lunge and Berl, *Ang.*, 1905, p. 1681.

[3] *S.S.*, 1912, p. 337.

cotton, nitro-glycerine and some of the more easily made nitro-aromatic compounds by-reactions only take place to a negligible extent. The revivification of the waste acid is carried out by adding nitric acid and C.O.V. or, more often, oleum. The calculations involved in ascertaining the quantities required are simple, but may present difficulties to those who are not familiar with the problem.

Example 1. The first step in the calculation is to ascertain the quantity of nitric acid required to raise the proportions of the acids to the proper figure. Thus suppose the waste acid and the required mixed acid have the compositions :

	Waste	Mixed
HNO_3	20·9	23
H_2SO_4	70·3	69
H_2O	8·8	8

Then to 100 parts of the waste acid it is necessary to add $70{\cdot}3 \times \frac{23}{69} - 20{\cdot}9 = 2{\cdot}53$ parts of HNO_3. The nitric acid, however, contains some water. Suppose it to be of 92·5 per cent. strength : then the quantity to be added is $\frac{2{\cdot}53}{0{\cdot}925} = 2{\cdot}73$ parts, which include 0·20 parts of water. The waste acid with this addition would then consist of

HNO_3	$20{\cdot}9 + 2{\cdot}5 = 23{\cdot}4$
H_2SO_4	$70{\cdot}3$
H_2O	$8{\cdot}8 + 0{\cdot}2 = 9{\cdot}0 = 8{\cdot}76$ per cent.
	$102{\cdot}7$

To this must be added a mixture of strong acids containing HNO_3 and H_2SO_4 in the same proportions. Suppose C.O.V. to be used, containing 95 per cent. H_2SO_4, together with the nitric acid of 92·5 per cent. strength. Then the mixture in the right proportions will consist of

HNO_3	23
H_2SO_4	69
H_2O	$23 \times \frac{7{\cdot}5}{92{\cdot}5} + 69 \times \frac{5}{95} = 5{\cdot}5 = 5{\cdot}64$ per cent.
	$97{\cdot}5$

The amount of 92·5 per cent. nitric acid in 100 parts of this strong mixture is $\frac{23}{0{\cdot}925 \times 0{\cdot}975} = 25{\cdot}5$, and of 95 per cent. C.O.V. $\frac{69}{0{\cdot}95 \times 0{\cdot}975} = 74{\cdot}5$.

To obtain a mixture containing 8 per cent. water from two, containing 8·76 per cent. and 5·64 per cent. respectively, they must be mixed in the proportions $(8 - 5{\cdot}64) : (8{\cdot}76 - 8) = 2{\cdot}36 : 0{\cdot}76$. Therefore to the 102·7 parts there must be added $102{\cdot}7 \times \frac{0{\cdot}76}{2{\cdot}36}$ parts of the strong acid mixture, and of this 25·5 per cent. is nitric acid and 74·5 per cent. is C.O.V. Hence the quantity of C.O.V. required is $102{\cdot}7 \times 0{\cdot}745 \times \frac{0{\cdot}76}{2{\cdot}36} = 24{\cdot}7$ parts, and of nitric acid $102{\cdot}7 \times 0{\cdot}255 \times \frac{0{\cdot}76}{2{\cdot}36} = 8{\cdot}4$ parts, to which must be added the 2·7 parts found before, making 11·1 parts of nitric acid in all. The quantities may now be checked by calculating the composition of the mixed acid obtained :

	HNO_3	H_2SO_4	H_2O
100 parts waste acid	20·9	70·3	8·8
24·7 ,, C.O.V.	—	23·5	1·23
11·1 ,, nitric acid	10·3	—	0·83
135·8 ,, mixed acid	31·2	93·8	10·86
100 ,, ,, ,,	23·0	69·0	8·0

If the quantity (135·8 parts) of mixed acid thus obtained be too great, part of the waste acid must be discarded, and the quantities of fresh acids reduced proportionally.

Example 2. If oleum be used the calculation is very similar. For this purpose it is convenient to reckon its strength as H_2SO_4. Suppose this is found by titration to be 114·1 per cent. H_2SO_4. This means that the addition of 14·1 grammes of water is required to convert 100 grammes of the oleum into 114·1 of H_2SO_4, and it contains $14{\cdot}1 \times \frac{80}{18} = 62{\cdot}7$ per cent. free SO_3. The percentage of water in it may be taken as — 14·1 per cent.

In the example considered above the composition of the acids used to reduce the percentage of water must be :

HNO_3	23
H_2SO_4	69
H_2O	$23 \times \frac{7{\cdot}5}{92{\cdot}5} - 69 \times \frac{14{\cdot}1}{114{\cdot}1} = -6{\cdot}66 = -7{\cdot}82$ per cent.
	85·34

The amount of 92·5 per cent. nitric acid in 100 parts of the mixture is $\frac{23}{0{\cdot}925 \times 0{\cdot}853} = 29{\cdot}2$ parts; and of oleum $\frac{69}{1{\cdot}141 \times 0{\cdot}853} = 70{\cdot}8$ parts.

To obtain a mixture containing 8 per cent. water from two containing 8·76 and — 7·82 per cent. respectively, they must be mixed in the proportions $(8 + 7{\cdot}82) : (8{\cdot}76 - 8) = 15{\cdot}82 : 0{\cdot}76$. Therefore to the 102·7 parts there must be added $102{\cdot}7 \times \frac{0{\cdot}76}{15{\cdot}82} = 4{\cdot}93$ parts of the strong acids. The quantity of oleum is $4{\cdot}93 \times 0{\cdot}708 = 3{\cdot}49$ and of the nitric acid $4{\cdot}93 \times 0{\cdot}292 = 1{\cdot}44$, to which must be added the 2·73 parts required to correct the proportions in the waste acid, making 4·17 parts of nitric acid. We have then:

	HNO_3	H_2SO_4	H_2O
100 parts waste acid	20·9	70·3	8·8
3·49 ,, oleum	—	4·00	– 0·50
4·17 ,, nitric acid	3·86	—	0·31
107·66 ,, mixed acid	24·76	74·30	8·61
100 ,, ,, ,,	23·00	69·00	8·00

Only 7·66 parts of fresh acid arer equired as compared with 35·8 when C.O.V. is used.

If the acids during the nitration process undergo practically no change except that due to the main reaction, and are not diluted by the subsequent addition of water, it is possible to calculate the composition of the waste acid with sufficient accuracy without analysing it, provided that that of the mixed acid be known. If c be the weight of cellulose or other substance nitrated, and a be the weight of nitric acid consumed, and y be the theoretical yield of the nitrated produce containing n per cent. of nitrogen, then

$$y = c + \frac{45}{63} a = c + \frac{5}{7} a$$

$$n = \frac{1400\,a}{63\,y} = \frac{200\,a}{9\,y} = \frac{1400\,a}{63\,c + 45\,a}$$

$$a = \frac{63\,cn}{1400 - 45\,n}$$

$$y = c + \frac{5}{7} a = c + \frac{9\,cn}{280 - 9\,n}$$

If w be the amount of water found in the reaction

$$w = \frac{18}{63} a = \frac{2}{7} a$$

In the special case of the manufacture of gun-cotton containing 13 per cent. N' $a = \frac{819}{815} c = 1{\cdot}005\,c$. That is to say, the weight of HNO_3 taking part in the reaction is practically the same as that of the cellulose.

Example 3. Take the case of a mixed acid of the composition:

H_2SO_4	70·5
HNO_3	21·0
HNO_2	0·6
H_2O	7·9
	100·0

To 100 parts of this are added 3·08 parts of cotton, which is thereby nitrated up to 13 per cent. N. This operation will consume 3·10 parts HNO_3 and produce $3{\cdot}10 \times \frac{2}{7} = 0{\cdot}886$ parts H_2O. The total quantity of waste acid is 97·79 parts, but the whole of this cannot be recovered.

It is to be revivified by the addition of nitric acid containing 92·1 per cent. HNO_3 and 0·6 per cent. HNO_2 and 7·3 per cent. H_2O, and oleum containing 19·2 per cent. free SO_3, equivalent to 104·32 per cent. H_2SO_4. We must first consider the replacement of the 3·10 parts HNO_3, which involves also the introduction of $3{\cdot}10 \times \frac{7{\cdot}3}{91{\cdot}1} = 0{\cdot}248$ parts of water and 0·02 parts HNO_2. The acid would then consist of

H_2SO_4	70·5	
HNO_3	21·0	
HNO_2	0·62	
H_2O.	9·03	= 8·93 per cent
	101·15	

The strengthening mixture consists of

H_2SO_4 .		70·5	
HNO_3 .		21·0	
HNO_2 .	$21{\cdot}0 \times \frac{0{\cdot}6}{92{\cdot}1} =$	0·14	
H_2O	$21{\cdot}0 \times \frac{7{\cdot}3}{92{\cdot}1} - 70{\cdot}5 \times \frac{4{\cdot}32}{104{\cdot}3} =$	− 1·26	= − 1·39 per cent.
		90·38	

The quantity of oleum to be added is $\frac{101{\cdot}15 \times (8{\cdot}93 - 7{\cdot}90) \times 70{\cdot}5}{(1{\cdot}39 + 7{\cdot}90) \times 90{\cdot}38 \times 1{\cdot}043} = 8{\cdot}40$.

And of nitric acid is $\frac{101{\cdot}15 \times (8{\cdot}93 - 7{\cdot}90) \times 21{\cdot}0}{(1{\cdot}39 + 7{\cdot}90) \times 90{\cdot}38 \times 0{\cdot}921} = 2{\cdot}83$, to which must be added the $3{\cdot}10 + 0{\cdot}25 + 0{\cdot}02 = 3{\cdot}37$ parts previously found, making 6·20 parts in all.

The revivification of the waste acid from 100 parts of the original mixed acid is as follows:

	H_2SO_4	HNO_3	HNO_2	H_2O
97·79 parts waste acid	70·50	17·90	0·60	8·79
8·40 ,, oleum	8·76	—	—	0·36
6·20 ,, nitric acid	—	5·71	0·04	0·45
112·39 ,, mixed acid	79·26	23·61	0·64	8·88
100 ,, ,, ,,	70·52	21·01	0·57	7·90

ALCOHOL, ETHYL

C_2H_5OH. Molecular weight 46·06

The alcohol used for the manufacture of smokeless powder should be of good quality, free from methyl alcohol and other injurious impurities. The French powder factories use commercial alcohol "bon goût" of strength 95 per cent. by volume (92·5 per cent. by weight, 66·7 over proof, specific gravity ·816), free from aldehydes, furfurol, higher alcohols, acids and organic bases and with not more than 0·005 g. residue from 100 c.c. As in the case of acetone any acidity is generally due to carbon dioxide and can be removed by boiling. After boiling the alcohol should be neutral. The U.S. Ordnance Department requires that the alcohol be tested for aldehydes by the ammoniacal silver nitrate test given above under "Acetone."

AMMONIUM OXALATE

$(NH_4)_2C_2O_4 + H_2O$. Molecular weight 142·11

This should be in the form of colourless crystals or white powder. When ignited or dissolved in water it should leave practically no residue. The solution should be neutral to litmus. It should contain no sulphates, chlorides or heavy metals. When dried at 100° for one hour the loss of weight should be about 12·7 per cent. The percentage of water in the air-dried salt remains constant at this figure unless the air be very dry or very moist.[1] It decomposes very slowly on heating to a moderate temperature: not sufficiently to affect seriously the heat test of an explosive containing it.

ANTIMONY SULPHIDE

(STIBNITE)

Sb_2S_3. Molecular weight 336·6

This material is found native in England and other countries; it has a density of 4·63 and the pure substance melts at 555°. At high temperatures it is volatile. The crude ore is refined by melting out the antimony sulphide, which then forms bluish-grey lumps with a metallic lustre and very brittle. It is also produced artificially, but in Germany it is forbidden to use in explosives the artificial product, or such as contains iron. It is absolutely essential that it should be free from sulphuric acid, as this has a very deleterious effect on the stability of explosive mixtures containing a sulphide and a chlorate, such as cap compositions. When treated with *aqua regia* it should not leave a residue of more than 0·5 per cent. It should be examined to see that it is not adulterated with sulphide of lead or iron, and that it contains little arsenic.

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[1] *See* P. V. Dupré, *Analyst*, 1905, p. 270.

Antimony Sulphide

The value of the substance as a constituent of cap compositions seems to be due largely to its hardness and crystalline form, which render the compositions sensitive to blows and friction.

For the determination of antimony sulphide in cap composition Brownsdon [1] has given the following method : After determining the fulminate by titration, the insoluble residue, containing the antimony sulphide and other substances, is filtered off on a small filter-paper, which is well washed and then transferred to a large test-tube. Five c.c. of strong hydrochloric acid are added and the contents of the tube boiled gently for a few seconds until the sulphide is dissolved and all the sulphuretted hydrogen has been driven off or decomposed. Three c.c. of a saturated solution of tartaric acid are then added and the contents of the tube washed into a conical flask of about 250 c.c. capacity. The solution is then nearly neutralized with sodium carbonate, excess of bicarbonate is added, and after the introduction of some starch solution the liquid is titrated with N/20 iodine solution. It is claimed that this method for small quantities of stibnite is both quick and accurate, and that the error does not exceed 0·0003 g.

AZIDES

(TRINITRIDES)

These are the salts of hydrazoic acid (azoimide), N_3H, which has about the same strength as acetic acid, but in many of its reactions resembles hydrochloric acid. It was first made by T. Curtius by the action of nitrous acid on hydrazine.[2] It is a colourless mobile liquid melting at —80° and boiling at 37°. Its vapour density corresponds to HN_3. It is a sensitive explosive.[3]

Sodium azide, NaN_3, molecular weight 65·03, can be made by first leading ammonia gas over metallic sodium, whereby sodamide is formed, and then leading nitrogen suboxide over the product at a temperature of 150° to 250° : [4]

$$2NaNH_2 + N_2O = N_3Na + NaOH + NH_3$$

It forms clear colourless hexagonal crystals, optically uniaxial and strongly doubly refracting. One hundred parts of water dissolve 41·7 parts at 17° ; 100 parts alcohol 0·315 parts at 16° ; it is insoluble in ether. It has a slightly alkaline reaction and a very salt taste. It is not exploded by blows, and by heat only at a very high temperature. It is neither volatile nor hydroscopic, and is not decomposed by evaporation of its aqueous solution. It has been proposed by the Winchester Repeating Arms Co. to use sodium azide as a constituent of priming charges together with potassium chlorate and antimony sulphide.[5]

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[1] *J. Soc. Chem. Ind.*, 1905, p. 381.

[2] *Ber.*, 1890, p. 3023.

[3] Dennis and Isham, *Ber.*, 1907, p. 458.

[4] Wislicenus, *B.*, vol. 25, p. 2084.

[5] U.S. Pat. 1,184,316 of May 23, 1916.

Lead azide, N_6Pb, molecular weight 291·3, is made by precipitating a solution of sodium azide with one of lead acetate. It is practically insoluble in cold water: a litre of hot water dissolves about 0·5 g. When such a solution cools, crystals are deposited which are very similar to those of lead chloride: these may be as much as a centimetre long, but such large crystals are extremely sensitive and have caused serious accidents. In a fine state of division the substance is comparatively safe, and is used for the manufacture of detonators (*see* Chapter XXXI).

Many other azides have been prepared (*see* Chapter XXXI), mostly from sodium azide, but only the lead salt appears ever to have been made on a considerable scale. Some of them, as for instance mercuric azide,[1] are dangerously sensitive.

Estimation. A solution of the azide is put into a flask connected with an azotometer. Attached to the stopper of the flask is a receptacle holding solid ceric ammonium nitrate or ceric sulphate, 2 to 3 grammes per 0·1 gramme sodium azide. The flask is immersed for some time in water of the same temperature as the azotometer, and then tipped up to mix the ceric salt with the solution. Nitrogen is generated according to the equation,

$$2N_3H + 2CeO_2 = 3N_2 + H_2O + Ce_2O_3$$

The solution should preferably be neutral. If chlorides be present it must be neutral, otherwise chlorine will be evolved.[2]

F. Raschig [3] has found that nitrogen is similarly evolved by the action of iodine on an azide, if a crystal of thiosulphate be present

$$2N_3Na + 2I = 3N_2 + 2NaI$$

If the solution contain any free mineral acid, sodium acetate must be added.

CELLULOSE

$(C_6H_{10}O_5)\,n$. Molecular weight 162·08 n

See Cotton

CHLORATE OF POTASSIUM

$KClO_3$. Molecular weight 122·56

This should be neutral and practically free from impurities. If made by the electrolytic method it always contains at least 0·05 per cent. of potassium bromate, and may contain as much as 0·6 per cent.[4] That manufactured by the old process does not contain this impurity. As bromate may have a deleterious effect on the stability of explosives made with it, especially if the

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[1] *See* L. Chenel, *P. et S.*, vol. 8, p. 23.

[2] E. Sommer and H. Pincas, *Ber.*, 1915, p. 1963.

[3] *Ber.*, 1915, p. 2058.

[4] A. Junk, *S.S.*, 1913, pp. 412 and 430.

Chlorate of Potassium

explosive also contain sulphur, an official order has been passed in Germany that chlorate for the manufacture of blasting explosives must not contain more than 0·15 per cent. bromate, for fireworks not more than 0·10 per cent., and for cap compositions none at all.

To detect the bromate, dissolve 2 grammes of the chlorate in 100 c.c. water, add 5 c.c. of a 10 per cent. solution of potassium iodide and 5 c.c. of normal hydrochloric acid and some starch solution. There should only be a slight blue colour after ten minutes. To determine the quantity, allow to stand for one hour in the dark and titrate with thiosulphate solution.

CHLORHYDRIN

(CHLORPROPYLENE GLYCOL) $C_3H_7ClO_2$

$CH_2Cl.CH(OH).CH_2(OH)$. Molecular weight 110·5

This substance may be made by heating glycerine with dry hydrogen chloride at a moderate temperature or with aqueous hydrochloric acid at a higher one. The reaction is assisted by the presence of acetic or other organic acid,[1] or of an ester, such as acetin.[2]

The product is heated *in vacuo* at about 70° to drive off the water and hydrochloric acid, then the temperature may be raised, and fractional distillation carried out *in vacuo*. A small quantity of dichlorhydrin distils over first, then monochlorhydrin, and finally unchanged glycerine. It is necessary to get rid of all the hydrochloric acid before raising the temperature, otherwise polymerization will take place. If the material is to be used for the production of low-freezing explosives, it is not necessary to submit it to fractional distillation, as the mixture of chlorhydrins and glycerine can be nitrated directly.

It may also be made by the action of chloride of sulphur on glycerine $2C_3H_8O_3 + 4SCl = 2C_3H_7ClO_2 + 2HCl + SO_2 + 3S$.[3] The sulphur can be made to separate out below by heating to 120°.[4]

Chlorhydrin has a specific gravity of 1·338 at 0°. Under atmospheric pressure it boils at 213° with some decomposition; under 18 mm. pressure it boils at 139°. It mixes in all proportions with water, alcohol and ether.

Dichlorhydrin

(DICHLORISOPROPYL ALCOHOL) $C_3H_6Cl_2O$.

$CH_2Cl.CH(OH).CH_2Cl$. Molecular weight 129·0

This is made in the same way as the mono derivative, only more hydrochloric acid or sulphur chloride is used and the treatment is continued longer.

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[1] Böhringer and Söhne, Ger. Pats. 197,308 of November 20, 1906, and 197,309 of December 15, 1906.

[2] *Chem. Fabr. Griesheim-Elektron*, Ger. Pat. 238,341 of March 18, 1908.

[3] Carius, Annalen, 122, 73; *Deutsche Sprengstoff A.-G.*, Ger. Pat. 201,230 of January 11, 1906. Ger. Pat. 229,872 of January 30, 1910.

Chlorhydrin

The statements as to its boiling-point and specific gravity are somewhat divergent, probably in consequence of impurities in some of the preparations. The mean value for the boiling-point is 176° to 177°. Under 10 mm. pressure it boils at 70°, and under 24·3 at 83° (Kahlbaum). The specific gravity is given as 1·383 at 0° and 1·367 at 19° by Markofnikof. It is soluble in 9 parts of water at 19° and 6 parts at 72°.

Chlor-dinitro-hydrin

(DINITRO-CHLORHYDRIN) $C_3H_5Cl(NO_3)_2$.

$CH_2Cl.CH(NO_3).CH_2(NO_3)$. Molecular weight 200·5

This is made from chlorhydrin by nitration with mixed acid in the same way as nitro-glycerine is manufactured from glycerine. According to Roewer[1] it is a yellowish liquid of slightly aromatic smell, soluble in ether, alcohol, acetone, chloroform and other organic solvents, but insoluble in water and acids. It mixes with nitro-glycerine in all proportions. Specific gravity 1·54 at 15°. When heated it begins to give off red fumes at 180°. It boils with slight decomposition at 190° to 193° at atmospheric pressure. Under 15 mm. pressure it boils at 121° to 123°, giving an almost colourless distillate. It is very insensitive to blows and could not be exploded by the 2 kg. falling weight even with a fall of 2 metres, nor yet by a 20 kg. weight. It is also insensitive to friction, but is readily detonated by fulminate. Roewer stated that the substance could not be made to freeze, but Kast[2] found that it solidified at a low temperature and melted again at temperatures varying from 1·5° to 6·8°: the divergence of these temperatures was probably due to the fact that the preparations did not consist of a simple substance, but of a mixture of different nitro-chlorhydrins.

Estimation.

Dichlornitro-hydrin or Nitro-dichlorhydrin, $C_3H_5Cl_2(NO_3)$ or $CH_2Cl.CH(NO_3).CH_2Cl$ may be made in the same way from dichlorhydrin. Its use in explosives has been protected by the Westfalisch-Anhaltische Sprengstoff A.-G.[3] It is described as a colourless liquid of specific gravity 1·459 at 15°.

Chlorhydrins and nitro-chlorhydrins are estimated by saponifying and determining the chlorine. This method is useful for determining dinitro-chlorhydrin in the presence of nitro-glycerine. Weigh out 1 gramme and saponify with 20 c.c. of a 15 per cent. alcoholic solution of caustic potash by boiling for fifteen minutes on a water bath under an inverted condenser. Evaporate off the alcohol and ignite. Dissolve in water, add a few drops of potassium permanganate solution to oxidize nitrite, acidify with nitric acid and precipitate with silver nitrate solution, or titrate by Volhard's method.

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[1] *S.S.*, 1906, p. 229.

[2] *S.S.*, 1906, p. 227.

[3] Ger. Pat. 197,404 of March 4, 1905.

Chlorhydrin

COTTON

(*See* Chapter XI)

Whether the cotton be in the form of waste, cop bottoms, linters or any other, it should be as free as possible from foreign matter, such as string, seed particles or pieces of metal. The moisture is determined by drying in an oven at 90° to 105°; it should not be more than 7 or 8 per cent. The oily matter is determined by extracting in a Soxhlet apparatus with ether; formerly as much as 1 per cent. was allowed to be present, but now the amount is generally restricted to 0·6 per cent. or less. To ensure that the cotton has not been over-bleached and is reasonably free from oxy-cellulose and other reducing substances the "copper value" should be determined: this depends to some extent on the exact procedure in carrying out the test, but a standard method has been worked out by Schwalbe. A determination of the "alkali oxide copper" will show whether or not the cotton has been mercerized. The loss on boiling with caustic alkali under specified conditions may also be ascertained, or the "wood-gum" may be determined.

Absorption of dye.

A measure of the amount of oxy-cellulose can also be effected by ascertaining the power to unite with basic dye-stuffs, such as fuchsine or methylene blue. Either the cotton may be treated with a dilute solution of the dye and well washed and the coloration compared with that taken by a standard sample under the same conditions, or the actual quantity of dye removed from solution may be ascertained. Lunge and Bebie [1] soaked 0·5 g. of the cotton in 150 c.c. of a 0·5 per cent. solution of methylene blue for an hour in a covered beaker standing on a boiling water-bath. When cold 100 c.c. were poured off and the colour was compared with that of the original solution by means of a colorimeter; 1 g. of pure cellulose took up 0·0012 g.

Copper value.

Schwalbe's method for the determination of the copper value of cotton [2] is as follows: 3 g. air-dry cotton are cut into small pieces and put into a wide-mouthed flask of 1·5 litre capacity, and 300 c.c. of boiling distilled water are poured over it. It is then boiled with constant stirring with a condenser immersed in the neck. No rubber should be used. Meantime 50 c.c. of alkaline Rochelle salt solution (346 g. Rochelle salt and 100 g. caustic soda in 1 litre) are heated to boiling, and to it are added 50 c.c. of copper sulphate solution (69·28 g. copper sulphate and 1 g. sulphuric acid to 1 litre) also boiling. The 100 c.c. of boiling Fehling's solution thus obtained is run into the flask through a side tube. From the moment when the contents are again boiling fully, the boiling is continued for fifteen minutes. Then the condenser and stirrer are removed and the contents of the flask are filtered off on a Buchner funnel and double filter paper of good quality, and washed until free from copper,

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[1] *Ang.*, 1901, p. 510.

[2] *Ber.*, 1907, p. 1347; *J. Soc. Chem. Ind.*, 1907, p. 548.

as shown by the potassium ferrocyanide test. The fibrous mass, together with the filter paper, is then placed in a porcelain basin and covered with hot water, 15 c.c. of a 6·5 per cent. solution of nitric acid are added, and it is digested until all the copper and cuprous oxide are dissolved. The cellulose is then filtered off again and washed with boiling water. Ammonia is then added to it, it is again acidified with nitric acid, and washed until free from copper. The filtrate is evaporated down to a convenient bulk, placed in a platinum dish, 1 or 2 c.c. of 10 per cent. sulphuric acid are added, and the copper is deposited electrolytically.[1] It is essential that the Rochelle salt be pure. When a blank test is done with it, it should give no precipitate or green colour. If it contain 0·4 per cent. of oxalate the results will be too high and unreliable.[2] The "copper value" is the percentage of metallic copper calculated on the dry cotton. The purest bleached cotton of high commercial quality has a copper value considerably less than 1, but specimens with values between 1 and 2 are fairly common. The following are the results given by materials that have been subjected to more or less drastic treatment:

	Copper Values	
Surgical cotton wool	1·64	1·8
Mercerized bleached Egyptian cotton yarn	1·9	1·6
Artificial silk (Glanzstoff)	1·1	—
Hydro-cellulose	5·2	5·8
Parchment paper	4·2	—
Bleached sulphite wood-pulp	3·9	3·9
Imitation ("greaseproof") parchment paper	3·5	3·0
Over-bleached sulphite wood-pulp	19·3	—
Oxy-cellulose from filter paper and bleaching powder	7·7	7·6
Bleached cotton rag-pulp (half-stuff)	6·5	5·6

Cotton waste for the manufacture of cordite is subjected in England to a simpler modification of this test. In a conical flask, the mouth of which is fitted with a wide glass tube to act as an air condenser, are placed 12·5 c.c. each of the copper sulphate and Rochelle salt solutions. The flask is immersed in boiling water for five minutes, and if the solution remain clear, 50 c.c. of boiling water are added and 1 g. of the cotton. The flask is then again immersed in boiling water for fifteen minutes. The cotton is filtered off on a Buchner funnel, washed with hot water, moistened with solution of Rochelle salt and washed again. The cotton is burnt off, the residue is ignited, then dissolved in nitric acid, evaporated to dryness, moistened with dilute nitric acid, washed into a flask, neutralized with sodium carbonate and acidified with acetic acid. Potassium iodide solution is then added and the liquid

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[1] C. G. Schwalbe, *Ang.*, 1910, p. 927.

[2] C. G. Schwalbe, *Ang.*, 1914, *Aufs.*, p 567

Cotton

is titrated with decinormal thiosulphate solution, of which 1 c.c. is equivalent to 0·0071 g. Cu_2O.

Hydrate copper value.

In addition to the direct determination of the cupric reducing value of cellulose, Schwalbe has described other applications of the reaction with Fehling's solution. The "hydrate copper value" represents in terms of metallic copper the amount of copper hydroxide absorbed by the cellulose from Fehling's solution in the cold. Three g. of the cellulose is immersed in 100 c.c. of Fehling's solution for three-quarters of an hour. It is filtered off and washed with boiling water. Then it is digested with dilute acetic acid, and in the extract the copper is then determined. For ordinary cotton this value is low, about 0·5, but is considerably higher for cotton that has been mercerized, or subjected to other treatment which increases its degree of hydration. C. Piest calls this figure the "alkali oxide copper value." It should be deducted from the ordinary copper value to obtain the true figure.

Another application of the reaction with Fehling's solution is the "hydrolysis difference value," which is the difference between the original cupric reducing value and the increased value obtained after boiling the sample for fifteen minutes with 5 per cent. sulphuric acid. This difference affords a measure of those portions of the cellulose, whether adventitious or pertaining to the complex, which are readily susceptible to hydrolysis by acids. Cellulose of a high degree of hydration, such as mercerized cotton, is hydrolysed more rapidly, and consequently shows greater difference values than ordinary cellulose, whilst hydro-cellulose, having already undergone acid hydrolysis, shows smaller differences.[1]

Wood-gum.

The matter dissolved by dilute caustic soda under specified conditions is often determined as throwing some light on the quality of the cellulose. Cotton waste for the manufacture of cordite is boiled with a 3 per cent. solution of caustic soda for one hour and the loss of weight is determined. The matters extracted consist partly of products formed by the breaking down of the cellulose itself, but partly of substances present originally, such as pentosans, hemi-celluloses and resins. Some of it can be reprecipitated, and the matter thus recovered has been termed "wood-gum." This is estimated as follows:

Fifteen g. of the dry cellulose are mixed with caustic-soda solution of exactly 5 per cent. strength, which is allowed to act for twenty-four hours with constant shaking at a temperature of 18° to 20°. The liquid is then pumped off and mixed with 100 c.c. of alcohol of 92·5 per cent. by weight and a little phenolphthalein; 9·5 c.c. of concentrated hydrochloric acid (specific gravity 1·19) are added, and normal acid is run in until the colour is just destroyed, and then a further 5 c.c. of normal acid is added. The liquid is allowed to stand twenty-four hours, then the precipitate is collected on a

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[1] *See* J. F. Briggs, *Analyst*, 1915, p. 116.

filter, which has been dried at 100° and weighed; it is washed with alcohol (92·5 per cent.) and then with ether, and dried at 100°.[1]

Viscosity. The determination of the viscosity of a solution in cuprammonium solution throws light on the state of the cellulose, but requires to be determined with considerable care to be of any value. Ost's method [2] is as follows: To prepare the cuprammonium solution 59 grammes of copper sulphate are dissolved in 3 litres of hot water and exactly precipitated with ammonia. The precipitate is decanted, filtered off and washed free of sulphates. Then it is put in a litre flask and made up to 1 litre with ice-cold ammonia of specific gravity 0·90. After standing for twenty-four hours the solution is filtered through asbestos. It only keeps for a few weeks. Air-dry cotton is weighed out equivalent to exactly 1 gramme of dry substance, and is placed in a stoppered flask with 50 c.c. of the cuprammonium solution. After a fixed period it is mixed with 50 c.c. of water and the time of flow through the viscometer is determined. This divided by the time of flow of the same volume of water is the viscosity. The viscosity falls rapidly at first and afterwards more slowly.

Acid value. The acid value is determined by boiling 3 g. of dry or 3·2 g. of air-dry cotton for fifteen minutes with 50 c.c. of water and 50 c.c. N/2 caustic soda solution on a sand-bath under a reflux condenser. The excess of alkali is then titrated with N/2 acid, using phenolphthalein as indicator. The consumption of caustic soda per 100 g. cotton is the acid value.[3] This figure is not used very much. Unlike the copper value it is much affected by the time of boiling and the strength of the reagent.

The following results are given by C. Piest: [4]

	Schwalbe copper value	Hydrate copper value	Vieweg acid value	Viscosity (Ost) solution diluted after	
				24 hours	48 hours
Normal cotton for nitrating .	1·64	0·55	1·86	24·3	16·5
Strongly bleached cotton. .	8·83	0·25	6·44	2·7	2·58
Very strongly bleached cotton.	16·2	0·52	9·22	2·23	2·12
Cotton treated with 5 per cent. soda for 24 hours at ordinary temperature. . . .	3·79	0·17	3·94	2·64	2·58
Mercerized cotton . . .	1·52	1·47	0·40	15·1	13·5
Hydro-cellulose . . .	4·13	traces	7·04	2·65	2·43

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[1] Kast, *Spreng- und Zündstoffe*, p. 919.

[2] H. Ost, *Ang.*, 1911, p. 1893.

[3] Vieweg, *Papier Zeit.*, 1909, p. 1352.

[4] *Ang.*, 1912, p. 2518.

Cotton

Ten samples of cotton for nitrating gave results within the following limits:

Wood-gum	0·59– 1·17
Copper value (Schwalbe)	0·70– 1·39
Hydrate copper value.	0·49– 0·57
Acid value (Vieweg)	0·40– 1·33
Viscosity (Ost) after 2 days	13·7 –34·1
,, ,, ,, 5 ,,	7·9 –24·0

All these determinations should preferably be made on material that has not been heated, as the results are liable to be affected thereby.

Determination.

Cellulose is determined in mixtures by extracting with ether, water and other solvents which do not attack it. If the cellulose be impure, wood meal for instance, complications arise in consequence of the solubility of resins and other impurities. It is necessary also to take into account the natural hygroscopic moisture in the cellulosic material; in the case of wood meal this is about 10 per cent.

In natural fibres, wood, etc., the true cellulose is determined by various more or less empirical methods, depending upon treatment with reagents which attack the non-cellulose more vigorously than true resistant cellulose. It is generally admitted that the method of Cross and Bevan [1] is the best for this purpose. This is carried out as follows: The material is dried in a vacuum desiccator and 5 grammes are weighed out and boiled for thirty minutes with a 1 per cent. solution of caustic soda, well washed on a gauze filter, squeezed to remove excess of water and placed in a beaker into which a slow stream of washed chlorine gas is passed, the temperature being kept at 0°. After thirty to sixty minutes' exposure it is removed, washed and heated to boiling with a 2 per cent. solution of sodium sulphite, then 0·2 per cent. of caustic soda is added and the boiling continued for five minutes. The cellulose is then filtered and washed. It is almost white, but may be finally bleached by immersion in dilute hypochlorite or permanganate solution (0·1 per cent.). It is then treated with sulphur dioxide, washed thoroughly, dried and weighed. The treatment with chlorine should be only just long enough to destroy the lignin, etc. Renewed treatment with chlorine should give no yellow colour, the material also should give no red colour with phloroglucin. A single treatment for thirty minutes suffices in the case of high-class material such as cotton or sulphite pulp, but wood shavings require to be treated with chlorine four or six times. This and some twenty other methods were examined by M. Renker,[2] who came to the conclusion that that of Cross and Bevan was the best. He proposed, however, to omit both the treatments with caustic soda. The omission of the caustic soda from the sulphite bath may be accepted as an improvement, but the preliminary treatment with alkali is necessary.[3]

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[1] C. F. Cross and E. J. Bevan, *Trans. Chem. Soc.*, 199.

[2] *Ang.*, 1910, p. 193; *Schriften des Vereins der Zellstoff- und Papierchemiker*, 2nd edition, Heft 1.

[3] J. F. Briggs, *Analyst*, 1915, p. 110.

Cotton

The French Government tests for non-cellulose in cotton by treating it with sulphuric acid of 75 per cent. strength. 155 c.c. of C.O.V. are mixed with 95 c.c. water and 10 g. of the cotton are immersed in it. Solution is complete in a few hours, but it is better to leave it for twenty-four hours. It is then poured into 1½ litres of distilled water and well stirred. The insoluble matter is filtered on a tared filter, washed, dried and weighed. It should not exceed 1 per cent.[1]

Dead fibres. "Dead" fibres may be recognized in cotton from the fact that they are doubly refractive, showing colours under the polarizing microscope. If a mica plate be inserted, the normal fibres remain bright in all positions, whereas the dead fibres, which are comparatively broad and flat, show black and white portions according to their direction.

Unripe fibres. Unripe fibres show less contrast than dead fibres under the polarizing microscope with the mica plate. The cuticle is but little developed, but the interior of the fibres is very rich in protoplasmic residues, which cause them to take up substantive dyes more intensely than the normal fibres. They are of about the normal breadth, but are not twisted.[2]

Specifications. For the manufacture of stable explosives the demands as to purity and chemical quality are somewhat severe, and the specifications are framed so as to ensure the use of only new material consisting mainly of mature, long-staple fibres, freed from seed residues ("motes") and carefully bleached. According to the chemical clauses of the British Ordnance specification[3] the cotton waste must not show more than the following amounts calculated on the dry substance:

Moisture	7·0	per cent.	
Oily matter	0·6	,,	
Loss on boiling one hour with 3 per cent. caustic soda	5·0	,,	
Reduction of Fehling's solution	1·0	,,	Cu_2O
Mineral matter	0·5	,,	

On dyeing with a basic dye-stuff, such as fuchsin, the fixation of colour must be slight and uniform and show no deeply dyed particles (seed residues) or fibres (oxycellulose).

C. Piest[4] states that the following figures should not be exceeded:

Copper value (Schwalbe)	1·0	per cent.	Cu
Fatty and waxy matters extracted by absolute alcohol	0·5	,,	
Wood-gum	2·0	,,	

According to H. Kast[5] wood cellulose, obtained in the form of paper, must not show more than:

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[1] D. Florentin, *S.S.*, 1913, p. 30.

[2] A. Herzog, *Chem. Zeit.*, 1914, 38, p. 1089; *J. Soc. Chem. Ind.*, 1915, p. 487.

[3] J. F. Briggs, *Analyst*, 1915, p. 118.

[4] *Papierfabrikant*, 1914, p. 860.

[5] *Spreng- und Zündstoffe*, 1909, p. 919.

Ash	1·0 per cent.
Soluble in ether	0·5 ,,
Wood-gum	1·0 ,,

calculated on the dry weight.

French specifications

The French State powder factories use three kinds of cotton.[1] Cotton waste No. 1 is a bleached waste from spinning and weaving mills using long staple cotton of American and Egyptian origin. The excess of oil is removed by extraction with carbon bisulphide. Waste No. 2 is a spinning-mill waste, not bleached, known as "bouts fins" (cop bottoms ?).

The third sort is linters, which must be quite free from cotton waste.

These must not show more than the following percentages:

	Waste No. 1	Waste No. 2	Linters	
Pickings (string, etc.)	2·0	2·0	0·02	per cent.
Ash	0·6	1·0	0·3	,,
Fat and oil	0·4	0·7	0·3	,,
Insoluble in sulphuric acid	1·0	—	—	,,
Moisture	—	—	6·0	,,
Free or oxidized chlorine	nil	nil	—	,,
Chlorides as NaCl	0·05	0·05		,,

U.S. specifications.

In the United States it is stipulated that the cotton used for the manufacture of military and naval powders shall be obtained from unspun waste or suitable short-fibred commercial cotton, whereas in England a proportion of spun cotton is preferred and linters are excluded. It must be bleached and purified and thoroughly washed to remove the purifying material and salts. It must not contain more than 0·4 per cent. of matter soluble in ether, nor more than 0·8 per cent. of ash. It must be of uniform character, clean and free from such lumps as will prevent uniform nitration. It should not contain more than traces of lime, chlorides and sulphates.[2]

DIPHENYLAMINE

$(C_6H_5)_2NH$. Molecular weight 169·2

This is a colourless crystalline substance melting at 54° and boiling at 302°; it is insoluble in water, but readily soluble in alcohol and ether. It is only a feeble base, and its salts are decomposed by water with separation of the base. Its solution in concentrated sulphuric acid gives with a trace of nitrous acid or other oxidizing agents an intense blue coloration. It is added to smokeless powder as a stabilizer (*see* Chapters XXI, XXXVIII, XXXIX).

It may be determined by saponifying the powder with strong caustic-soda solution, until its structure is destroyed, and then distilling with steam, until

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[1] Buisson, *Problème des Poudres*, p. 17.

[2] E. M. Weaver, *Notes on Military Explosives*, 3rd edition, 1912, p. 188.

Diphenylamine

the distillate no longer gives a coloration with sulphuric acid containing a little nitric acid. The distillate is then shaken out with ether and the ethereal solution is dried with calcium chloride and evaporated. The residue is dried over sulphuric acid and weighed. If camphor or other volatile non-basic substance be present, the diphenylamine may be precipitated from the ethereal solution with dry chlorine gas, the precipitate filtered off in a Gooch crucible, washed with ether, dried for thirty minutes at 65° and weighed. Multiplication by the factor 0·83 gives the free diphenylamine.[1]

Dreger determines it as tetrabrom-diphenylamine.[2] The ethereal solution obtained as above is warmed with alcohol until the ether has been driven off; then bromine is added drop by drop until there is an excess. The liquid is diluted with twice its volume of water and boiled until the alcohol and bromine have been driven off and the volume has been reduced to half. The precipitate of tetrabrom-diphenylamine is filtered off, washed with warm water and dried at 98° to 100° until the weight is constant. Multiplication by the factor 0·3487 gives the weight of diphenylamine.

In France diphenylamine, together with nitroso-diphenylamine, is determined in Poudre B as follows:[3] The powder is cut into small pieces and 10 grammes are placed in a Jena glass flask of 1 litre capacity, together with 500 c.c. of a 6 per cent. solution of caustic soda. The flask is connected through a condenser with another flask on which is a mark showing 300 c.c. The contents of the litre flask are boiled. The powder is destroyed by the soda and the nitroso diphenylamine is converted into diphenylamine, which passes over in the steam together with the rest of the diphenylamine. When 300 c.c. of distillate have been collected, the condenser is washed out with 50 c.c. of chloroform, which is added to the contents of the receiver. To this are also added 2 c.c. of 10 per cent. hydrochloric acid, and by means of a burette 40 c.c. of bromine water. The flask is shaken vigorously every five minutes for half an hour, by which time the bromination is complete, and the chloroform layer has dissolved the product and the excess of bromine, except a small portion, which colours the water a pale yellow. About 10 c.c. of 20 per cent. solution of potassium iodide are then added, and the liquid is titrated with $N/10$ thiosulphate, some starch solution being added before the end. The nitro-derivatives of diphenylamine are attacked somewhat by the soda, but they give no diphenylamine.

Diphenylamine for the manufacture of Poudre B must be either in the form of small crystals, white or slightly yellow, or in fused crystalline lumps of uniform colour, slightly yellow. It must not contain chloride or carbonate of ammonium or sodium, as their presence would indicate that the substance had been badly purified. Its melting-point must be between 52° and 54°.

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[1] Kast, *Spreng- und Zundstoffe*, p. 958.

[2] *S.S.*, 1909, p. 123.

[3] Buisson, *Problème des Poudres*, p. 127.

Diphenylamine

It must not contain more than 0·001 per cent. of aniline or toluidine, as these primary amines attack nitro-cellulose.[1] These are detected by adding the powdered diphenylamine to a solution of bleaching powder.

ETHER

(ETHYL ETHER, ETHYL OXIDE)

$(C_2H_5)_2O$. Molecular weight 74·10

Pure ether has a specific gravity of 0·7191 at 15°/4° and boils at about 34·4° under 760 mm. It tends to take up a little moisture from the air, however, whereby the density is slightly increased, but the boiling-point is only slightly affected.[2] If it contain a little alcohol it can dissolve more water. It is made by heating alcohol with strong sulphuric acid. The ether as it forms distils off. It is condensed, washed to remove sulphur dioxide and other impurities, and redistilled.

For the manufacture of smokeless powders pure ether is required made from good commercial alcohol. The U.S. Government specification[3] requires that it shall contain no impurities other than small quantities of water and ethyl alcohol. It must be clear and colourless, with the characteristic odour. Its acidity calculated as acetic acid is not to exceed 0·006 per cent., it must not leave more than 0·002 per cent. residue when evaporated down, and its specific gravity at 20° C. is to be between 0·717 and 0·723.

If ether be exposed to light and air, peroxides are liable to be formed, and these have an injurious effect on the stability of nitro-cellulose gelatinized with the solvent. They are tested for by shaking 10 c.c. of the ether with 1 c.c. of 10 per cent. potassium iodide solution in a completely filled glass-stoppered bottle; neither the ether nor the potassium iodide solution should be perceptibly coloured after standing for an hour in the dark.

To test for sulphur compounds shake 20 c.c. of the ether with a globule of mercury for two minutes in a glass-stoppered bottle. The bright surface should not be tarnished, nor should a black precipitate form.

Methylated ether is made from methylated spirit by the action of strong sulphuric acid. In addition to some alcohol and a little water, it contains dimethyl and methyl-ethyl-ether, which have greater solvent power for nitro-cotton, but boil at considerably lower temperatures than ethyl ether. The specific gravity of methylated ether varies from 0·72 to 0·73 or higher, the variation being principally due to the amount of alcohol and water in it.

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[1] Buisson, *loc. cit.*, p. 43.

[2] *See* Marshall, *Trans. Chem. Soc.*, 1906, p. 1384.

[3] Weaver, *Military Explosives*, 3rd edition, p. 189.

FULMINATE OF MERCURY

$Hg(ONC)_2$. Molecular weight 284·6

(*See also* Chapter XXXI)

Manufacture. Mercury is cleaned by squeezing it through wash-leather, 0·5 kg. is weighed out into a glass flask and 5·5 kg. of nitric acid (specific gravity 1·36) are added. When all the mercury has dissolved, the solution is allowed to cool, and then is poured into a large glass flask containing 5 kg. of alcohol of 90 per cent. strength, which has been warmed previously, if necessary, to a temperature of 20° or 25°. A reaction sets in almost at once accompanied by effervescence and the temperature of the liquid rises rapidly to about 80°; then the reaction moderates, but the temperature goes on rising slowly to 83°. Crystals of fulminate are seen to form, and the upper part of the flask is filled with white fumes. After about ten minutes red fumes appear, the evolution of gas becomes much more rapid, and the solid is formed faster; the temperature rises to about 86°, but its height depends to some extent on the outside temperature and other circumstances. Then the reaction moderates, and the fumes in the reaction vessel becomes paler again. The total time of reaction is twenty to twenty-five minutes. The contents of the flask are then poured into water and washed by decantation until practically all the acid has been removed. In different factories the proportions of acid and spirit to mercury are varied somewhat.[1] but it is essential that a large excess both of nitric acid and alcohol be used, otherwise the yield of fulminate is much reduced; if only 6·5 parts of 60 per cent. spirit be used to 1 part of mercury, no yield at all is obtained. The yield is generally 1·2 to 1·3 of fulminate from 1 of mercury, whereas according to theory there should be 1·42.

The fumes given off in the reaction should be drawn off by means of a good draught, because if they condense in the reaction vessel, they have a deleterious effect on the product. They are conveyed into stone-ware bottles or tubes, where they are condensed as far as possible; they are very poisonous and inflammable. The condensate. which consists of ethyl nitrate and nitrite, aldehyde, unaltered alcohol, etc., is in some factories utilized to mix with fresh quantities of alcohol.

Fulminate can also be made if for alcohol be substituted various other substances containing the group $CH_3.CHO$, such as aldehyde, paraldehyde, metaldehyde, dimethyl- and diethyl-acetal. On the other hand no fulminate is obtained from methyl alcohol, formaldehyde, propyl alcohol or butyl aldehyde, nor from glycol or glyoxal.[2]

Pure fulminate is white, but the product obtained as just described is grey in colour or, if methylated spirit has been used instead of "commercial

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[1] *See* Solonina, *S.S.*, 1910, p. 42.

[2] L. Wöhler and K. Theodorovits, *Ber.*, 1905, p. 38.

Fulminate of Mercury

alcohol," brown, the coloration being due to traces of resinous substances formed in the reaction. If 1 part of metallic copper and the same quantity of hydrochloric acid be added to the nitric-acid solution just before it is poured into the alcohol, "white" fulminate is obtained, but analysis shows that this contains more instead of less impurity than the grey fulminate. The whiteness is apparently due to bleaching of the coloured bodies, and not to their destruction.

After the fulminate has been washed by decantation, it is collected on a muslin filter, and the washing is continued with distilled water until acidity can no longer be detected with litmus-paper. In some works it is washed with alcohol of 82 to 85 per cent. strength.

Properties.

To the naked eye fulminate looks like fine sand: under the microscope it is seen to consist of crystals generally 0·01 to 0·1 mm. long. They are octohedra, usually truncated, only the smaller crystals being fully developed. The specific gravity is 4·42 or 4·39,[1] but when merely shaken down the apparent density is only about 1·75. In detonators it is usually compressed to a density of about 2·5. A litre of water dissolves 0·7 g. at 13°, 1·7 at 49°,[2] and about 8 g. at 100°.[3] From water it is said to crystallize with half a molecule of water [4] in small fibrous crystals. Mercury fulminate dissolves readily in an aqueous solution of potassium cyanide, from which it can be reprecipitated with strong acid; pyridine also dissolves it easily and it can be recovered from the solution again by pouring into water. R. Philip, however, found that the best method for purifying small quantities in the laboratory is to dissolve it in ammonia, filter rapidly, and neutralize with 30 per cent. acetic acid.[5] Fulminate is also soluble in solutions of thiosulphate, especially if acid be added, but it is decomposed thereby. Concentrated hydrochloric acid also dissolves it with decomposition.

The residue left when the substance is dissolved in any of these solvents should be small, and when examined under the microscope, this residue should be free from particles of metallic mercury. The fulminate should be free from oxalates and chlorides.

Estimation.

Brownsdon pointed out that when fulminate is treated with a solution of sodium thiosulphate, it dissolves with formation of alkali, and the fulminate can be determined by titration with standard acid.[6] This reaction has been investigated by Philip,[7] and by G. Peace and myself. The results are in agreement with the equation:

$$Hg(CNO)_2 + 2Na_2S_2O_3 + 2H_2O = HgS_4O_6 + C_2N_2 + 4NaOH.$$

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[1] Berthelot and Vieille, *Ann. Chim. Phys.* (5), vol. 21, p. 509; Solonina.

[2] Hollemann, *Rec. Trav. Chim.*, 1896, p. 159.

[3] Solonina, *S.S.*, 1910, p. 68.

[4] Schischkoff, *Lieb. An.*, 97, p. 54.

[5] *S.S.*, 1912, p. 223.

[6] *J. Soc. Chem. Ind.*, 1905, p. 381.

[7] *S.S.*, 1912, pp. 109, 156, 180, 198, and 221.

The cyanogen, of course, reacts with the caustic soda to form cyanide and cyanate :

$$C_2N_2 + 2NaOH = NaCN + NaCNO + H_2O$$

but on adding acid cyanogen is regenerated :

$$NaCN + NaCNO + H_2SO_4 = C_2N_2 + Na_2SO_4 + H_2O.$$

If the alkaline solution be allowed to stand, the alkalinity gradually diminishes, due to the formation of sulphate and sulphocyanide from the tetrathionate, cyanide and cyanate :

$$HgS_4O_6 + NaCN + NaOCN + NaOH = HgSO_4 + 2Na_2SO_4 + NaSCN + H_2O.$$

This secondary change is restrained by a large excess of thiosulphate, but more effectively by potassium iodide. In the absence of iodide and with only a moderate excess of thiosulphate half the alkalinity disappears in about one hundred minutes at 30°, and practically the whole of it in twenty-four hours. With ten times as much potassium iodide as fulminate of mercury in the solution only 12 per cent. of the alkalinity disappears in one hundred minutes, and if the titration be carried out at once, the loss is quite small. If the fulminate be dissolved with excess of the iodide and a known volume of standard thiosulphate, the excess of thiosulphate can also be titrated with standard iodine solution after the alkali has been neutralized with standard acid, and so a double estimation is effected on the same quantity of material. To this Philip has given the name of the " Bofors method " ; it is carried out as follows :

Fifty c.c. of N/10 thiosulphate solution is pipetted into a beaker, and about 3 g. of pure potassium iodide is dissolved in it ; 0·3 g. of the fulminate is rapidly washed in and the liquid is agitated until it is dissolved. The fulminate may be moistened beforehand with alcohol to prevent particles floating on the surface or forming lumps. A few drops of methyl-orange solution are now added and the solution is titrated with N/10 sulphuric acid ; then a little starch solution is added and it is titrated with N/10 iodine solution. The whole operation can be carried out in six minutes. The solutions may be standardized either by the ordinary methods, or upon fulminate of mercury that has been purified by means of ammonia and acetic acid, as above. One c.c. N/10 thiosulphate is equivalent to 0·01423 g. mercury fulminate, and 1 c.c. N/10 acid to 0·007115 gr. As a rule the fulminate shows the same percentage in both titrations, but in abnormal samples the acidimetric titration sometimes gives a higher result. A good grey fulminate will show 98 to 99·5 per cent. of the pure substance ; white fulminate generally gives results slightly lower, and fulminate purified with ammonia and acetic acid shows 100 per cent. within the limits of experimental error.

A blank determination should be made and corrections applied accordingly. Potassium iodide is liable to contain iodate which affects the results of the titrations both with acid and iodine. The titration with iodine is but little affected by time, even in the absence of potassium iodide.

On keeping, fulminate is gradually converted into non-explosive compounds. The unaltered fulminate in a composition can be estimated by the above method, as the decomposition products do not react with the thiosulphate. The quantity of fulminate originally added to the mixture can be ascertained by determining the mercury by one of the usual methods.

FULMINATE OF SILVER

AgONC. Molecular weight 149·9

This is made in much the same way as fulminate of mercury, but as it is far more sensitive, it is only prepared in very small quantities at a time. It is too sensitive for use as an igniter or detonator, but it is employed in the manufacture of toy fire-works, such as bonbon snaps, throwdowns and crack shots. A thousand of these must not contain more than 15 grains of fulminate of silver. In England only 1 grain per person is allowed in work-rooms.

FULMINATING MERCURY AND SILVER

(NITRIDES OF MERCURY AND SILVER)

Hg_3N_2. Molecular weight 629·8
Ag_3N ,, ,, 337·6

These compounds, which must not be confused with the fulminates, are made by treating the corresponding oxides with ammonia. They are very sensitive explosives. Oxide of gold forms a similar compound.

GLYCERINE

(GLYCEROL) $C_3H_8O_3$.

$CH_2OH.CHOH.CH_2OH$. Molecular weight 92·08

For the analysis of crude glycerine, standard methods have been adopted by an International Committee, which published a report in January 1911.

The glycerine used for the manufacture of nitro-glycerine is all distilled (*see* Chapter XV). The pure substance is colourless and has a specific gravity of 1·265 at 15·5° compared with water at the same temperature. Dynamite glycerine usually has a pale amber colour, and the specific gravity should not be less than 1·261. When diluted with 2 volumes of water, the solution should be clear; with litmus it should give no decided red or blue coloration; it should be practically free from sugars, fatty acids, salts of heavy metals and other impurities. Sugars and other carbonizable substances are tested for by adding to the glycerine in a test-tube an equal volume of concentrated sulphuric

Glycerine

acid and allowing to stand for an hour; there should be no decided darkening of colour. Sugars may also be tested for by heating 5 g. with 50 c.c. water and a few drops of hydrochloric acid on a water-bath for half an hour, rendering alkaline with caustic soda and adding Fehling's solution: no yellowish red cloud or precipitate should appear. Heavy metals are detected by adding sulphuretted hydrogen water; calcium, with ammonia and ammonium oxalate solution; sulphates, with barium chloride; oxalates, with calcium chloride; and chlorides, with silver nitrate solution. If, in the last test, the solution blackens, it indicates the presence of reducing substances; the test is made more delicate by the addition of a little ammonia. In none of these tests should there be indications of more than traces of the impurities.

Residue may be tested for by evaporating down at 100° and drying in an oven at this temperature, until the weight is constant. An easier way is to put 10 grammes in a crucible, ignite it and allow it to burn away. The residue should not exceed 0·25 per cent. Afterwards it may be ignited to determine the ash, which should not exceed 0·05 per cent. In the ash, chlorides can be estimated by extracting with water and titrating with silver nitrate solution. There should not be more than 0·01 per cent. calculated as NaCl. Combined fatty acid may be determined by mixing 100 grammes with 10 c.c. of N/10 caustic soda solution and 200 c.c. of boiling water, corking the flask and heating it on a water bath for an hour, then cooling and titrating with N/10 acid, using phenol phthalein as indicator. The percentage of glycerine can be determined directly by means of the acetin method. It should show not less than 98·5 per cent.

A nitration test is sometimes carried out on a small quantity in the laboratory,[1] but the results thus obtained may be quite different from those yielded by the same glycerine on the manufacturing scale. It is therefore better to try a sample drum in the nitro-glycerine factory.

The following are the results of analysis of some representative samples of dynamite glycerine:

	per cent.	per cent.	per cent.
Salt	0·003	0·001	0·001
Ash	0·0032	0·001	0·002
Carbonaceous residue	0·04	0·012	0·018
Free acid	0·0042	0·0058	—
Combined acid	0·045	0·025	0·022
Specific gravity at 15°	1·2641	1·2632	1·2642

GLYCERINE NITRATES (LOWER)

Mono- and dinitro-glycerine were investigated by Will.[2]

Dinitro-glycerine may be made by adding 10 parts of glycerine to 33 parts

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[1] *See* Escales, *S.S.*, 1906, p. 23; Novak, *ibid.*, p. 191.

[2] *Ber.*, 1908, p. 1107; *S.S.*, 1908, p. 324.

Glycerine Nitrates

of nitric acid (specific gravity 1·5) and then pouring on to a minimum of ice. The greater part of the product separates as an oily layer, but is mixed with some trinitro-glycerine. The yield obtained by Will was about 65 per cent. of the theoretical, but Schüpphaus got 80 to 81 per cent.[1]

Another method is to nitrate 100 g. glycerine with 500 g. mixed acid of the composition : HNO_3, 23 per cent., H_2SO_4, 68 per cent., H_2O, 9 per cent., at a temperature not exceeding 20°. The mixture is poured into ten times its volume of water, the few oily drops of trinitro-glycerine are separated, and the dinitro-compound is shaken out with ether. The ethereal solution is neutralized by shaking with 5 per cent. soda solution ; the ether is distilled off, and the residue dried over sulphuric acid. The yield is about 45 per cent. of the theoretical.

It may also be prepared from trinitro-glycerine by dissolving in sulphuric acid, diluting with water and shaking out with ether.

There are two possible isomerides, $CH_2(NO_3).CH(OH).CH_2(NO_3)$ and $CH_2(NO_3).CH(NO_3).CH_2(OH)$, and the product was indeed found to be a mixture. By cooling, about two-thirds of a crystalline modification could be separated, the crystallization being much facilitated by introducing a crystal from a previous experiment. The residual oil, which probably contained both isomers, could not be made to crystallize. The crystals were found to have the composition $3(C_3H_6O_7N_2) + H_2O$. The water was retained on recrystallizing from water, alcohol, ether and benzene, but was given off when the substance was dried over sulphuric acid or in the air at 40°. It was reabsorbed from the air at the ordinary temperature. The liquid portion contained about the same proportion of water (calc. 3·19 per cent.). The crystalline dinitrate readily yields well-defined esters, in which the third hydroxyl group has been replaced by another radicle. Thus the benzoyl ester is obtained by treating it with the calculated quantity of benzoyl chloride and alkali in aqueous solution ; it is insoluble in water, crystallizes well from organic solvents and melts at 67°. The p-nitro-benzoyl ester crystallizes still better, and melts at 94°.

The liquid dinitrate has not the same tendency to give well-defined esters. The p-nitro-benzoyl ester was, however, obtained crystalline ; it melts at 81° and differs from the compound yielded by the crystalline dinitrate, in that it is readily soluble in hot alcohol, whereas the latter is only slightly soluble. This affords a means for estimating the amount of the two nitrates present in a mixture.

Mononitro-glycerine can be made by nitrating glycerine, carefully neutralizing the remaining acid, and allowing to stand. After a time the mononitrate separates in crystalline form. Crystallization can be accelerated by cooling and rubbing with a glass rod. It melts at 58° to 59° when purified by re-

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[1] *S.S.*, 1910, p. 361.

crystallization. It does not contain water of crystallization. Unlike the dinitrate it is not explosive. With calcium nitrate it forms a compound $4C_3H_5(OH)_2(NO_3) + Ca(NO_3)_2$, which, after being recrystallized several times from alcohol, melts at 117°.

The mononitrate obtained as above is the α-compound with the nitro-group attached to one of the end carbon atoms, $CH_2(OH).CH(OH).CH_2(NO_3)$, as is shown by the fact that it yields both dinitrates when nitrated further. Moreover, the same compound, melting at 58°, is obtained by the prolonged action of hot water on mono-nitro glycid $CH_2.CH.CH_2(NO_3)$.

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The β-mononitrate $CH_2(OH).CH(NO_3).CH_2(OH)$ was also obtained from the mother liquors from the α-nitrate. It melts at 54°. On further nitration it yields only the fluid dinitrate, together with trinitrate. The following Table gives the principal properties of these compounds:

	Glycerine	Mononitrate	Dinitrate	Trinitrate
Spec. grav. (15°) . .	1·27	1·40	1·47	1·60
Melting-point . .	17	α 58° β 54°	α-hydrate 26° β-hydrate liquid.	Labile mod. 2·2° Stable mod. 12·2°
Boiling-point (15 mm.) .	150–160°	155–160° both isomers	About 145° both isomers	Evaporates rapidly at 160°
Solubility in water at 15°	Unlimited	70 per cent.	7·7 per cent.	0·16 per cent.
Sensitiveness, 2 kg. falling wt.	0	0	Dry 7–10 cm. Crys. or liquid with 3 per cent. H_2O 30 cm.	Less than 4 cm.
Heat of explosion. .	—	—	Dry 1250 cal.	1600 cal. (?)
Heat of combustion (H_2O liquid)	4317 cal.	α 2812 cal.	α dry 2088 cal. α crys. 1986 cal. β 2055 cal.	 1570 cal. —
Gelatinizing power .	—	nil	Good	Good
Hygroscopicity . .	80 per cent.	50 per cent.	11 per cent.	0·2 per cent.

The following additional particulars have been given by Blochmann:[1]

		Dinitrate	Trinitrate
Heat test (zinc iodide-starch paper at 70°) .		8 mins.	More than 20 mins.
Ignition point		167°	180°
Velocity of detonation, liquid . . .		1525 m. sec.	1525 m. sec.
,, ,,	gelatinised . . .	3320 m. sec.	7000 m. sec.
,, ,,	with 25 per cent. Guhr	4290 m. sec.	6820 m. sec.

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[1] *Der Bergbau*, August–September, 1905: *S.S.*, 1906, p. 80.

A great disadvantage of dinitro-glycerine is its solubility in acids and water, which makes its separation and purification difficult. It is more liable to become solid than the trinitro-compound and is more difficult to thaw. Hence it does not appear to possess any advantages except as an addition in small proportion to nitro-glycerine in order to lower its freezing-point.

Dinitro-glycerine is a constituent of Tremonit and Ammon-tremonit, explosives that are authorized for conveyance by rail in Germany.[1]

In admixture with trinitro-glycerine the dinitro-compound may be estimated from a determination of the nitrogen in the nitrometer, or by determining the nitric radicles by Silberrad's method (p. 737).

GRAPHITE

C. Atomic weight 12·005

Graphite used in the manufacture of smokeless powder should be quite free from sulphides and free acid, and should contain only a trace of silicate. It should be in the state of fine powder, and should have had acidity removed by washing with soda. Graphite made electrically is liable to contain sulphuric acid.[2]

HEXANITRO-ETHANE

$C_2(NO_2)_6$. Molecular weight 300·1

This substance is prepared as follows: Calcium picrate is treated with calcium hypobromite giving bromopicrin, $CBr_3.NO_2$, and this, when treated with potassium cyanide and nitrite, is converted into the potassium salt of tetranitro-ethane $C_2(NO_2)_4K_2$, which when nitrated with mixed acid gives hexanitro-ethane. It is insoluble in water, only slightly soluble in cold alcohol, but readily in other organic solvents, from which it separates in colourless crystals, which melt at 142° with some decomposition. It is not acid to litmus, and is somewhat less volatile than camphor, which it resembles in smell. It is not very sensitive to blows or friction, about the same as sodium picrate, but can be detonated by itself, and when mixed with oxidizable substances forms powerful explosives. It is however unstable; in 20 hours at 50° it showed red fumes.[3]

KIESELGUHR

(GUHR, INFUSORIAL EARTH)

(*See* Chapter XXV)

Before use it is ignited and passed through a fine sieve. When mixed with three times its weight of nitro-glycerine it should form a dry plastic mass, from which the nitro-glycerine cannot be pressed out. Under the microscope

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[1] *See also* Volpert, *S.S.*, 1906, p. 167.

[2] A. Dupré, *A.R.*, 1904, p. 28.

[3] W. Will, *Ber.*, 1914, p. 961: Germ. Pat. 281,906, of 1913.

Kieselguhr

it is seen to consist of diatoms; the absorptive power depends largely on the proportion of tubular forms. It should be free from gritty matter, such as sand, so that when rubbed between the fingers it feels quite smooth, like flour, and should be capable of absorbing at least four times its weight of nitro-glycerine without appearing wet. The percentage of organic matter should not exceed 2 per cent., nor should there be an undue amount of moisture. It absorbs moisture from the air very readily, however, and requires to be redried at a temperature of 200° to 300° before use. It should be free from acid and alkali and the nitro-glycerine extracted from dynamite made with it should stand the regulation heat test. As the ignited guhr is non-volatile and insoluble in water and organic solvents, its determination presents no difficulty. It can be dissolved almost entirely in strong caustic soda solution.

MERCURY

Hg. Atomic weight 200·6

Metallic mercury, and such of its compounds as are liable to be reduced to the metallic state during the manufacture and storage of explosives, have a very decided masking effect on the Abel heat test, and for this reason the addition of such mercury compounds is absolutely prohibited in England. In Germany it has been customary to add sufficient mercuric chloride to nitro-cottons to entirely mask the test. The late Dr. Dupré and his sons have worked out spectroscopic tests to be applied to the various explosives; in doing so they have kept in mind that minute traces of mercury are liable to be introduced into explosives during the course of manufacture from the sulphuric acid used and other sources, but that it is only desired to detect mercury in such quantities and in such forms as would affect the heat test. It is calculated that $\frac{1}{1000}$ mg. of mercury is sufficient to mask the heat test, but there would be no great difficulty in devising tests that would detect much smaller quantities. Since they published their methods in *A.R.*, 1907, p. 17, many other chemists have described processes for effecting the same object, but in many cases the essential point just mentioned has not been taken into account by them. The following are the Duprés' methods:

Home Office tests for mercury.

The apparatus consists of two stoppered tubes of about 20 c.c. capacity, joined by a capillary-tube. To one stopper is attached a tube fitted with a good tap. All the grinding must be done very perfectly so as to keep a vacuum for some hours even at a slightly raised temperature. About the centre of each tube, electrodes, contained in tubulars slanted up so as to prevent the entrance of explosive material, are attached. The parts of the tubes below these tubulars are filled with the substance to be examined, the stoppers are replaced, and the tube exhausted by means of a good pump (not a mercury pump). The parts of the tube containing the explosive are then immersed

Mercury

in hot water (about 90°), and a discharge from a powerful induction coil (6-inch spark) passed through it. The capillary tube is then examined end on: if a condenser is used, the spectrum is greatly intensified. If mercury or a volatile mercury salt be present even in very minute quantities, the characteristic lines of the mercury spectrum are seen in addition to those of any other gases that may be present, such as nitrogen, oxygen, and hydrogen. The spectrum of nitrogen may be eliminated by passing a stream of hydrogen through the cold tube before exhausting; after exhaustion, practically only the spectra of mercury, if present, hydrogen and oxygen will then be seen. The hydrogen and oxygen spectra can never be eliminated, as it is impossible to get rid of the last traces of moisture, but this does not in any way interfere with the spectrum of mercury.

The lines relied on for proving the presence of mercury are the two yellow, the green, and the violet of the following wave-lengths: the yellow 5790 and 5769, the green 5461, and the violet 4359. The presence of mercury is not certified, unless all these lines are seen. All the apparatus used, tube, connexions, etc., must be carefully tested to prove the absence of mercury before each test is carried out.

Ungelatinized gun-cotton.

In the case of nitro-cotton about 2 g. of the nitro-cotton, carefully dried at a temperature not exceeding 120° F. (49°), are introduced into the special vacuum tube, and the test is carried out as described above.

Blasting gelatine, geglignite, etc

With blasting gelatine, gelignite, etc., about 4 g. of the explosive are ground up with French chalk, introduced into the vacuum tube and tested as above. If the explosive contains a considerable amount of moisture, the introduction of a piece of calcium chloride above the explosive in each limb may be of considerable value. Blank experiments must be made with the chalk used before the test is carried out.

Cordite.

In order to apply the test to cordite, 15 g. of the cordite are ground so as to pass through the finest sieve of the heat-test set, and extracted with ether for two hours. The flask is then removed, and a carefully cleaned flask substituted; fresh ether is introduced and the extraction continued for a further ten hours. The ether is then distilled off. and the flask carefully dried at a low temperature. The flask is washed out with several quantities of distilled water, a little hydrochloric acid being added to the first boiling. The washings are put into a previously ignited platinum dish, and the solution electrolysed overnight, using the dish as anode and a coil of platinum or gold wire as kathode. Two Leclanché cells are used in series for the electrolysis. The wire is then washed with water and acetone. dried at a low temperature, dropped into a clean narrow test-tube (3 inches by $\frac{3}{8}$-inch). and the part of the tube containing the wire strongly ignited. The bottom of the tube is cut off after removing the wire, and the remainder dropped into the vacuum tube and tested for mercury, as already described.

Hard gelatinized nitro-cotton preparations.

Hard gelatinized nitro-cotton preparations are treated exactly as cordite, unless the explosive contains nothing which is soluble in ether, other than a mercury salt, in which case the preliminary two hours' extraction with ether is omitted.

Specially delicate tests.

If an ungelatinized nitro-cotton has to be tested for very minute traces of soluble mercury salts, any desired quantity can be extracted with ether, and treated as described above for hard gelatinized nitro-cotton explosives.

Metallic mercury.

All the above tests, in which extraction by ether is employed, are of course only tests for soluble mercury-salts, not for metallic mercury. The following very delicate test may be used for blasting gelatine or any other explosive when only metallic mercury is sought.

Fifteen grammes or any other quantity, according to the degree of delicacy required, are ground up with French chalk and introduced into a stoppered bottle. A piece of silver foil is ignited in a combustion tube, through which a slow current of hydrogen is passed. This foil is then placed in a glass spoon on top of the explosive, and the bottle is tightly stoppered and kept at a temperature of 90° to 100° for ten to fifteen hours. The silver foil is then treated in the same way as the coil in the cordite test.

Considerable difficulty has been experienced by firms who have been using mercury in their explosives in the past in getting their plant free from all traces of it. Even six months after the last addition of mercury the explosive still contains enough very seriously to affect the heat test. In this connexion it may be of service to point out what an extremely minute amount of mercury may affect the result. From quantitative experiments it was found that even 0·001 mg. of mercury can combine with as much iodine as would be liberated by an average sample of blasting gelatine in the five minutes after the standard tint on the test-paper was reached, or, in other words, is capable of masking the heat test to the extent of five minutes.

With reference to the rejection of explosives on account of their containing mercury, it has been suggested that the main objection to its use, viz., its effect on the heat test, might be overcome by introducing a piece of silver foil into the tube during the test. It was alleged that the mercury was thus retained entirely by the silver and that the true test of the explosive was obtained. This point was therefore investigated, but it was found that, although the effect of the mercury on the test-paper was undoubtedly counteracted and a test that had been much prolonged by the presence of mercury was considerably shortened, yet the silver itself had a considerable masking effect, probably due to the absorption of the acid vapours by the silver. It was therefore considered that, although the above test might be useful as a supplementary test for the presence of mercury, it could not be considered to remove the objections to the use of mercury in explosives. The use of gold foil was also suggested, but although preferable to silver for use with nitro-cottons, in that its masking effect is considerably less, yet, as it decomposes nitro-glycerine vapour, it cannot be used with nitro-glycerine explosives [1]

Microscopic test for mercury

Hargreaves and Rowe, of the Government Laboratory, South Australia, have worked out a process in which the microscope is used instead of the spectroscope.[2] One hundred g. of blasting gelatine, gelatine dynamite, gelignite, etc., are ground up in a mortar with 100 g. of purified French chalk, the grinding being done in small quantities at a time. The mixture is placed in a flask in a water-oven and connected by glass tubing passing out of the water-oven to a Woulff's bottle or other absorption apparatus containing 50 c.c. of water and 75 c.c. of strong sulphuric acid, and the whole is gently aspirated, while the flask is heated in the bath to the temperature of boiling water. In about two hours the mercuric chloride will be transferred to the dilute sulphuric acid in the absorption apparatus. The solution is then subjected to electrolysis, a pure gold kathode and platinum anode being used. The current required is about 0·5 ampere, or less, at a pressure of 2 volts. The deposition of the mercury on the gold is complete in a few hours, but the current may conveniently be left going all night. When the quantity of mercury is large, the gold kathode will be seen to be coated with mercury, and it may be weighed, and the test thus made quantitative, but, as a rule, there will not be sufficient deposit to be visible. The gold foil is removed from the electrolyte, while the current is still running, washed in distilled water, then in alcohol, dried, rolled into a cornet, and inserted into a glass tube 6 mm. in diameter, sealed at one end and expanded at the other and ground flat to fit closely against a glass microscope slide. The glass tube is fitted in a hole in a stout brass plate and then very gently heated, after a dry microscope slide has been placed on top. A sublimate will be obtained on the glass slide, and care must be taken not to raise the temperature sufficiently to revolatilize this. The slide on being examined under the microscope at a magnification of about 250 diameters by transmitted and reflected light will show globules of metallic mercury of large or small size, according to the skill with which the heating has been conducted. If the globules are very small, they may not be readily recognized as mercury, but under the conditions of the method any small opaque dots showing brilliant specks by reflected light must be mercury, and a repetition of the test will probably show larger globules. A similar method has been adopted in West Australia.[3]

In the German Ordnance factories the following test is applied:[4] 2 g. of moist nitro-cotton containing 25 to 30 per cent. water are put into a test-tube 16 mm. wide and 125 mm. long, closed with a cork, through which passes

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[1] *See also* Florin, *S.S.*, 1911. pp. 21 and 63.

[2] *J. Soc. Chem. Ind.*, 1907, vol. 26, p. 813.

[3] *See A. and E.*, August. 1908; *S.S.*, 1909, p. 191.

[4] Kast, *Spreng- und Zündstoffe*, p. 929.

a glass rod covered 5 mm. below the cork with a strip of gold leaf 12 mm. wide. The test-tube is placed in a water-bath heated to 80°, so that the moisture condenses in the neighbourhood of the gold leaf. The heating is continued for at least four hours. If mercury be present, small greyish-white specks will appear on the gold, and for confirmation these should be converted by means of iodine into iodide of mercury. It is advisable to carry out three or four tests simultaneously.

MINERAL JELLY

(PETROLEUM JELLY, VASELINE)

This is a semi-solid product obtained from petroleum: after the greater part of the oil has been distilled off, the residue is drawn from the still, and the paraffin-wax is removed from it as far as possible by filtration. It is a very complex mixture of substances, mostly hydrocarbons, some of which are unsaturated. Mineral jelly is a constituent of cordite and a number of other smokeless powders, and is also added sometimes to blasting explosives.

It has no definite melting-point, and yet in order to obtain a uniform product it is necessary to determine it by some arbitrary method; it may be done as follows: A rod is provided with a platinum loop somewhat resembling those used for the heat test, but rather larger. A thin filament of the jelly is laid across the loop near its upper end, and the rod, together with a thermometer, is introduced into a test-tube, which is placed in a beaker of water. The temperature is gradually raised, and the thermometer is read when the jelly runs down to the bottom of the loop. This is taken as the melting-point. For the manufacture of cordite, it is required that it shall not melt below 30° (86° F.). Another method is to cover the bulb of a thermometer with a thin film of the substance and then make a slit in the film with a knife. The bulb is then immersed in a beaker of water which is gradually heated. The temperature at which the slit opens is taken as the melting-point. To determine the fatty acids 10 grammes are dissolved in 100 c.c. of pure ether and then precipitated again by the addition of 100 c.c. of absolute alcohol: after standing overnight in the dark, 50 c.c. are drawn off and titrated with N/10 caustic soda, using phenol phthalein as indicator. The mineral jelly should not require more than 0·03 per cent. KOH. The end point is the first appearance of purple in the meniscus. Its flash-point by the close test should not be below 204° (400° F.), and its specific gravity at 37·8° (100° F.) not less than 0·87. It must be free from scales or specks, and from acidity towards litmus. Heated on a boiling water-bath for twelve hours in an open basin it must not lose more than 0·2 per cent. When burnt off it must leave practically no residue.

Mineral jelly is readily soluble in ether, petroleum ether, and various other organic solvents, but it is only slightly soluble in alcohol; in a mixture of

4 parts methyl-alcohol and 1 part water it is practically insoluble, as also in acetic acid. These last solvents may be used to separate it from nitro-glycerine in the ether extract obtained in the analysis of a complex explosive. After distilling off the ether, some 80 per cent. methyl-alcohol is added to the residue in the flask, which is then heated on a boiling water-bath. The liquid is allowed to settle for a minute or two, and is then decanted through a small filter or directly into a clean beaker. After repeating this operation about four times the mineral jelly is quite free from nitro-glycerine. After the first washing, it is advisable to heat the flask again before adding more alcohol, in order to cause the mineral jelly to adhere to the glass. If any globules of mineral jelly get into the filter or beaker, they must be washed free from nitro-glycerine, and then transformed back into the extraction flask, if necessary with the aid of a little ether. After drying in a steam-oven the mineral jelly may be weighed in the extraction flask.

In old cordites the mineral jelly is often partly converted into substances which are soluble in the 80 per cent. methyl-alcohol, and consequently the percentage found is low. In such cases the nitro-glycerine may be destroyed by heating with an alcoholic solution of caustic soda. The liquid is then neutralized with sulphuric acid, diluted with water and extracted with ether. The extract is evaporated down and the residue dried and weighed.

MOISTURE

(VOLATILE MATTER)

All explosives that have been wholly or partly gelatinized retain more or less of the organic solvent used. In the case of the larger sizes of Cordite M. D. it amounts frequently to more than 1 per cent., and nitro-cellulose powders, in which there is no nitro-glycerine, generally contain several per cent., which it is impracticable to drive off in the drying stoves, as it is retained by the colloid with great obstinacy.

In the case of explosives not containing nitro-glycerine, camphor, or any other constituent that is slightly volatile, the material is ground and sifted, and 2 g. are weighed out on to a watch-glass and dried in an oven at a suitable temperature to constant weight. As a rule, it is not advisable to take for this purpose material that has been ground more finely than is laid down in the directions for the heat test, because the very fine material loses some of its volatile matter during grinding, sifting and weighing. The temperature of the oven is usually somewhere between 65° and 100°. Explosives that are thoroughly stable will withstand the latter temperature for several hours without undergoing a sufficient amount of decomposition to affect the results. In the case of unstable materials a lower temperature must be employed, however, and in extreme cases the drying should be carried out at the ordinary temperature in a vacuum desiccator.

American method.

In order to avoid losses during grinding and weighing, in the United States the nitro-cellulose powder is merely cut up and is degelatinized by dissolving in ether-alcohol and reprecipitating with water.[1] Slices are cut from at least 5 average grains in the case of large-calibre powders; with smaller powders whole grains may be taken or slices may be cut from a number. The sample thus obtained is thoroughly mixed and 1 g. is weighed out. This is dissolved in 150 c.c. of ether-alcohol (2 : 1), and when solution is complete, the nitro-cellulose is precipitated by the gradual addition of a suitable amount of water, and the mixture is evaporated on a steam-bath. When evaporation is apparently complete, it is dried for one hour at 95° to 100°, or in a vacuum drier at 50° and weighed. The loss of weight corrected for the residue in the solvent and water used is called the "total volatiles, as packed."

"Moisture" is also determined. This is estimated by drying at least 5 grains, weighing not less than 20 g., for two hours in a vacuum drier at 50° to 60°. The difference between the "total volatiles" and the "moisture" is called the "residual solvent." In the American small arms powder the "total volatiles" must not exceed 3·15 per cent.

French method.

In France a similar precipitation method is used for determining the volatile matter in Poudre B.[2] But if it contain diphenylamine, which is slightly volatile, the estimation is made by drying *in vacuo* at the ordinary temperature.

Determination of water.

For the determination of the water only, in substances which also contain acetone and other volatile compounds, Dupré recommends the use of calcium carbide.[3] The ground material is put into a tube 1 cm. wide and 10 cm. long and covered first with a layer of dry sand and then with a layer of carbide 5 cm. high. The tube is connected to a nitrometer filled with saturated brine, and heated in a water-bath to 100°. The moisture reacts with the calcium carbide producing acetylene. The volume of gas evolved is slightly less than that calculated, when known volumes of water are present: it varies somewhat with different samples of carbide. The coefficient of the carbide may be determined by an experiment with a known weight of pure ammonium oxalate, which contains 12·67 per cent. of water of crystallization. The carbide used by Dupré gave 1 c.c. for 0·001725 g. water.[4] If the smokeless powder be exposed to the air, the amount of water in it varies with the hygrometric state of the atmosphere and therefore with the season of the year.[5]

Moisture in nitro-glycerine explosives.

In determining the moisture in nitro-glycerine explosives the difficulty to be overcome is owing to the fact that nitro-glycerine itself is slightly volatile. But investigations carried out at the Royal Gunpowder Factory, Waltham Abbey, by Dupré and Marshall, showed that the difficulty could be overcome by the use of a special apparatus, consisting of an aluminium dish covered

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[1] Weaver, *Military Explosives*, 1912, p. 200.

[2] Buisson, *S.S.*, 1913, p. 288.

[3] *Analyst*, 1906, p. 213.

[4] *See also* Huntly and Coste, *J. Soc. Chem. Ind.*, 1913, p. 63; and Campbell, *ibid.* p. 67.

[5] *See* Hansen, *S.S.*, 1911, p. 461.

Moisture

with a glass cone, so as to leave only a very slight space between them for the escape of the vapour of water and organic solvent.[1]

The apparatus (Fig. 154) is warmed and allowed to stand for half an hour in a desiccator to acquire constant weight. Then 5 g. of the sample are placed in the aluminium dish, the glass cone is put over it, and the whole is weighed. The apparatus is then stood upon a metal plate heated below by boiling water or steam: the top of an ordinary boiling-water oven is suitable. Here it is allowed to stand until the weight is practically constant. In the case of Cordite, Mark I, or ballistite, or blasting gelatine, an hour is sufficient; Cordite M. D. requires two hours. The apparatus is then removed to the desiccator, allowed to stand for half an hour and weighed. The loss of weight is the amount of moisture (volatile matter) in the explosive taken. Any nitro-glycerine that is driven off from the powder by the heat is condensed on the glass cone; the loss of nitro-glycerine from the apparatus is less than 0·01 per cent. The results are very consistent. The material should be ground and sifted in the same manner as is laid down in the instructions for the heat test.

FIG. 154.
Apparatus for the Determination of Moisture in Nitro-glycerine Explosives

The same method can be used for explosives containing nitro-toluenes. Mono-nitro-toluene is not very much more volatile than nitro-glycerine, and consequently there will be but little loss. Dinitro-toluene is less volatile than nitro-glycerine, and trinitro toluene, if free from mono- or di-nitro-toluene, or other volatile impurity, loses no appreciable weight even when dried on open watch-glasses. The moisture can also be determined in celluloid by this method, but in this case there is a slight loss, as camphor is more volatile.

The U.S. Bureau of Mines determines the moisture in dynamites by placing 2 g. of the explosive on a 3-inch watch-glass in a desiccator containing strong sulphuric acid at about 20°, and weighing after three days. An approximate determination may be made by desiccating in this way for twenty-four hours and multiplying the loss in weight by the factor 1·111. Or the loss of weight in a vacuum desiccator in twenty-four hours may be taken without correction as the approximate amount of moisture.[2]

NITRATES

Ammonium Nitrate

NH_4NO_3. Molecular weight 80·05

Ammonium nitrate has a specific gravity of about 1·72 at the ordinary

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[1] *See* A. Marshall, *J. Soc. Chem. Ind.*, 1904, vol. 23, p. 154.

[2] *Bureau of Mines Bulletin*, No 51, p. 29.

temperature. It is very soluble in water and consequently very deliquescent. It crystallizes in a number of different forms at different temperatures, and these are converted one into the other on heating, the reverse changes taking place on cooling again. The following are the different forms and the temperatures of conversion :

Tetragonal	
	− 16° C.
α-Rhombic	
	+ 32·5°
β-Rhombic	
	83°
Rhombohedral	
	125°
Regular	
	165°
Liquid	

On further heating it begins to decompose, and at 210° the evolution of gas is considerable. The change from α-rhombic to β-rhombic is accompanied by an expansion of 3·3 per cent. and an absorption of heat of 5·02 Calories per kg. That from β-rhombic to rhombohedral by a contraction of 1·4 per cent. and an absorption of 5·33 Calories per kg. The further change to the regular system is also attended by expansion and an absorption of 11·86 Calories. In passing through these transition temperatures the crystals are necessarily disintegrated.

Ammonium nitrate, being volatile at a moderate temperature, may be tested for residue by heating in a crucible. That made by neutralizing ammonia solution with nitric acid, or by the double decomposition of ammonium sulphate and calcium nitrate (Norwegian nitrate), should be almost free from residue, but if made by the double decomposition of ammonium sulphate and sodium nitrate it may contain several per cent. of the latter salt. This is not a very harmful impurity in blasting explosives as it is a powerful oxygen carrier. The nitrate, should, however, be practically free from other salts. These may be detected by testing for sulphates, chlorides, etc., in the usual way. The substance should be white and entirely soluble in water, giving a solution neutral to litmus. It should contain no ammonium nitrite, which is unstable. To test for this impurity 1 gramme of the ammonium nitrate is dissolved in 20 c.c. of water, and to it are added 1 c.c. of a 16 per cent. solution of sulphuric acid and 1 c.c. of a freshly prepared 0·5 per cent. solution of metaphenylene-diamine hydrochloride : no yellow or yellowish-brown colour should develop. The solution of metaphenylene-diamine hydrochloride should be colourless before use, and if necessary must be rendered so by warming with ignited animal charcoal.

The percentage of moisture should not exceed 1. As the salt is very hygroscopic, especially if impure, and easily decomposed at a high temperature, it is best to dry it in a vacuum desiccator. Or the ammonium nitrate may be estimated by determination of the nitrogen in a nitrometer, or of the ammonia by distillation with caustic soda and titration with acid. The moisture is then obtained by difference.

Ammonium nitrate may be determined in complex explosives by the methods just mentioned.

It can be detonated by means of a priming cartridge of a violent explosive, but only partially by a fulminate detonator. It is not usually considered an explosive when unmixed with oxidizable material.

Saltpetre

(NITRE, POTASSIUM NITRATE)

KNO_3. Molecular weight 101·1

(*See* Chapter IV)

Impurities.

Chlorides should always be tested for, as their presence greatly increases the tendency of the gunpowder or other explosive to deliquesce. In England not more than 0·005 per cent., reckoned as sodium chloride, is allowed; in Germany and France about twice as much. The test is carried out by adding a few drops of silver nitrate solution to a concentrated solution of the saltpetre of known strength, and the opalescence is compared with that given by a solution containing a known amount of sodium chloride.

Sulphates are tested for with barium chloride, calcium with ammonium oxalate and ammonia, and magnesium with ammonium phosphate after removing calcium. The substance should dissolve in water practically without residue, and the solution should be neutral to litmus. To test for sodium nitrate, make a hot saturated solution, allow to cool, dip a platinum wire in the mother liquor and put it in the Bunsen flame; there should be no yellow coloration of the flame. Moisture may be determined by heating to incipient fusion in a crucible; good saltpetre contains practically no moisture.

Saltpetre should contain no chlorate, which greatly increases the sensitiveness of explosives. Perchlorates are not so injurious; Dupré found that even 1·21 per cent. perchlorate, although it depressed the temperature of ignition of gunpowder 56°, did not appreciably increase the sensitiveness to friction and impact.[1] The amount of chlorate and perchlorate can be determined by heating 10 to 20 g. of the saltpetre for an hour at 545° in a nickel crucible in a Gilbert furnace. The salt is then dissolved in water and filtered, and the chloride is titrated with silver nitrate by Mohr's method, or more accurately with ammonium sulphocyanide by Volhard's method. The result must be corrected for chloride present in the saltpetre before heating.[2]

The following method for the determination of chlorates is given in *P. et S.*, 11, 1902, p. 63 :10 g. of saltpetre are dissolved in 50 or 60 c.c. of water,

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[1] *A.R.*, 1902, p. 25.

[2] Dupré, *J. Soc. Chem. Ind.*, 1902, p. 825.

and sufficient silver nitrate is added to precipitate the chlorides. The filtrate is then heated to 90°, and a solution of lead nitrate slightly acidified with nitric acid is added. Turbidity indicates the presence of chlorate, and the amount is estimated by using standard solutions of saltpetre and chlorate. In France the saltpetre must not contain more than 0·01 per cent. chlorate, or 0·1 per cent. perchlorate. Indian saltpetre does not contain these impurities, but that made by the conversion of sodium nitrate from Chile saltpetre often contains a small proportion.

If the nitrate is to be added to a nitro-glycerine explosive its heat test is sometimes taken in conjunction with nitro-glycerine. The nitrate is finely powdered and 0·32 gramme (5 grains) is placed in a test tube with 2 c.c. of nitro-glycerine. The heat test should not be lower than that of the nitro-glycerine alone.

Estimation. In black powder the saltpetre is readily determined, because it is soluble in water and the other two constituents are not. The finely ground charcoal has, however, a tendency to pass through the filter. A convenient method is to weigh out 2 g. into a 100 c.c. flask, dissolve in water, make up to the mark, allow the liquid to settle, draw off 20 or 25 c.c. with a pipette, evaporate to dryness, dry in a steam-bath and weigh. The saltpetre may then be examined for chlorides, etc. If there be other substances present soluble in water, the saltpetre can generally be estimated in the water extract by means of the nitrometer.

Sodium Nitrate (Chile Saltpetre)

$NaNO_3$. Molecular weight 85·0

That used for the manufacture of nitric acid should contain at least 96 per cent., as determined by the nitrometer or the Schlösing method, and not more than 0·75 per cent. of sodium chloride.

The following are analyses of commercial nitrate :[1]

Sodium nitrate	94·17	94·25
Potassium nitrate	1·76	1·25
Sodium chloride	0·93	1·18
Sodium iodate	0·01	0·02
Potassium chlorate	0·28	0·24
Magnesium sulphate	0·22	0·30
Magnesium chloride	0·29	0·34
Calcium sulphate	0·10	0·04
Insoluble	0·14	0·17
Moisture	2·10	2·21
	100	100

The chloride is specially injurious, because in the distillation the chlorine reacts with the nitric acid producing lower oxides of nitrogen.

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[1] M. R. Lamb, *Engineering and Mining Jour.*, 1910.

If the nitrate is to form a constituent of an explosive it should be purified by recrystallization several times. It may be tested by the same methods as are used for saltpetre, but the requirements as to purity are not so severe.

NITRO-CELLULOSE

(*See also* Part IV, Chapters X, XII, and XIII)

Properties.

The true specific gravity is given by Mosenthal as 1·65 to 1·68.[1] Buisson states that that of gun-cotton (CP_1) is 1·674, and of soluble nitro-cellulose (CP_2) 1·662.[2] Ordinary compressed blocks containing much water and air have a specific gravity of 1·0 to 1·2, but if highly compressed for blasting purposes it may be as high as 1·4. The compressed material resembles wood pulp. When it has been gelatinized with a solvent it resembles horn. It is slowly saponified by alkalies. It is reduced to cellulose by potassium and ammonium hydrosulphides, sodium stannate, sulphides, polysulphides, and thiocarbonates. It is somewhat hygroscopic. Will showed that if n is the percentage of nitrogen in a sample of nitro-cotton, and h the percentage of moisture it takes up in almost saturated air at 25°, $n + h = 14{\cdot}6 \pm 0{\cdot}1$. Even good nitro-cellulose decomposes at all temperatures, giving off carbon monoxide and nitrogen oxides. The rate of decomposition is doubled for every increase of 5° (Will).

When gun-cotton is to be used for the manufacture of other explosives it is usually moulded in hydraulic presses into blocks of various shapes containing 30 to 40 per cent. of water. When used by itself as a blasting explosive it is compressed strongly until it is as hard as hard wood and contains about 20 per cent. of moisture. That used by the British Government is a nitro-cotton containing 12·8 to 13 per cent. of nitrogen mixed with a little phenol and calcium carbonate to prevent decomposition. Small cylinders of the same material, but dried, are employed as primers for firing charges of wet gun-cotton. Nitrated cotton yarn impregnated with rubber solution is also used as a priming charge for certain sorts of ammunition.

Nitrogen.

According to the strength and composition of the acids and other conditions of nitration, nitro-celluloses can be obtained with very different proportions of nitrogen and differing in many of their properties. It is possible in the laboratory to prepare a gun-cotton containing 14 per cent. of nitrogen, which almost agrees with the formula for the trinitrate $C_6H_7(NO_3)_3O_2$, but this compound is very unstable and breaks down even on standing at the ordinary temperature for a few weeks, leaving a lower nitrate. On the manufacturing scale it is hardly practicable to produce a nitro-cellulose containing more than 13·5 per cent. of nitrogen, and commercial gun-cotton seldom contains more than about 13 per cent. The gun-cotton used for making cordite is specified to contain 12·8 to 13·1 per cent. Nitro-cottons used for making some other

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[1] *J. Soc. Chem. Ind.*, 1906, vol. 26, p. 443.

[2] *Problème des Poudres*, p. 30.

Nitro-Cellulose

smokeless powders for sporting and military purposes generally contain percentages of nitrogen from 12·4 up to 12·8 per cent. Collodion cotton for blasting gelatine contains 12·0 to 12·3 per cent.; for celluloid, varnish, and artificial silk still lower nitrates are used. Various writers have endeavoured to classify nitro-celluloses according to their chemical formulae; assuming the celluloid molecule to be of some particular size, $C_6H_{10}O_5$ or $C_{12}H_{20}O_{10}$ or $C_{24}H_{40}O_{20}$, they have divided the nitro-celluloses into tri- and di nitrates, or penta-, tetra-, and tri-nitrates, etc., but as no definite line can be drawn between the different classes, and products can be obtained with any desired percentages of nitrogen, it is better to specify the nitro-celluloses according to their percentages of nitrogen, solubility in ether-alcohol, and other properties.

Detection of nitro-cellulose.

Practically all propellents contain nitro-cellulose wholly or partly gelatinized. Many of them consist practically entirely of nitro-cotton, and most of them contain at least 50 per cent. The form of cellulose used is almost invariably cotton, but wood cellulose has been employed in the manufacture of Schultze powder and some others. Colloided nitro-cellulose can be recognized by its hard, tough nature; unless mixed with liquid material, such as nitro-glycerine, it is as tough as horn. It may be distinguished from other substances by the fact that it is insoluble in water, alcohol, or ether, but soluble in acetone and ethyl acetate. The various nitro-cottons are distinguished from one another, after isolation, by the percentage of nitrogen and of matters soluble in a mixture of alcohol and ether.

Ungelatinized nitro-cellulose can be recognized by the structure of the fibres, which is almost the same as that of the unnitrated material. There is, however, a distinct difference in colour when the fibres are examined in polarized light.[1]

Estimation of nitro-cellulose.

Nitro-cellulose is usually estimated by extracting the explosive with one or more of the solvents in which nitro-cellulose is insoluble, and then weighing the residue of nitro-cellulose. The first extraction is nearly always with ether, and in many cases no further extraction is needed. If mineral nitrates are present, a further extraction with water is necessary, and in many cases an extraction with benzene is required to remove organic substances. About 2 g. of the explosive are weighed out into a filter-paper or thimble and extracted in a Soxhlet with ether (specific gravity 0·72). The filter-paper and contents are then dried in a water-oven to constant weight, and the weight of the filter-paper or thimble is deducted. The material used for this analysis should be so finely ground that it passes through the finer sieve of the nest used for the heat test. This material should be allowed to soak in the ether all night and then extracted with it for about two hours.

In some cases, if the percentage of nitrogen in the nitro-cellulose is known, it may be estimated indirectly by a nitrogen determination.

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[1] *See* H. Ambronn, *Kolloid-Zeits.*, vol. 13, 1913, p. 200.

Nitro-Cellulose

Determination of nitrogen.

The estimation of nitrogen in gun-cotton is generally carried out by means of a Lunge nitrometer provided with a cup and graduated from about 100 to 150 c.c. It is filled with mercury, the bottom of the tube being connected by means of rubber tubing with canvas insertion to a compensating tube. The gun-cotton is dried in a water-bath to constant weight, 0·5 g. or more is weighed out, according to the percentage of nitrogen, precautions being taken that moisture is not absorbed during the weighing, as the material is very hygroscopic. It is then transferred to the cup of the nitrometer, and 5 c.c. of concentrated sulphuric acid are added. The material is stirred from time to time with a small glass rod until it dissolves, which takes about half an hour. Then it is allowed to run into the nitrometer, and is rinsed in several times with sulphuric acid, using for this purpose 10 c.c. The bulb is then shaken vigorously so as to bring the mercury and acid into intimate contact. After a short time nitric oxide is evolved. The shaking is continued for about three minutes until the evolution is practically complete. Then the nitrometer is allowed to stand until the acid and mercury have separated from one another and the shaking is repeated for about one minute. After standing for about half an hour to cool, the volume, temperature and barometric pressure are read, the volume is corrected to N. T. P. and the percentage of nitrogen in the gun-cotton is calculated. In this as in all operations with the Lunge nitrometer the result depends to some extent on the exact method of shaking, and it is only after some practice that the operator can obtain results approaching the theoretical. Beginners generally obtain results which are too low.

Berl and Jurrissen carry out the reaction with acid and mercury in a separate vessel and claim that thereby a more accurate result is obtained. In the case of gelatinized smokeless powders they oxidize first with chromic acid (*see* below under "Nitro-Compounds"). If the powder contain mineral jelly or diphenylamine or other substance that absorbs oxides of nitrogen, the usual nitrometer method gives low results.

The Schultze-Tiemann method is also used extensively in many laboratories for the estimation of nitrogen. It usually gives results 0·1 or 0·2 per cent. higher than the Lunge nitrometer. It is specially useful for the analysis of gun-cottons that have not yet undergone purification by boiling, as the nitrometer gives very low results for these. They evidently contain some unstable impurities, which interfere with the reaction of the mercury. The following are the details of the method as it is carried out at the Dartford factory of Messrs. Curtis and Harvey:

0·5 g. of the dry nitro-cellulose and 30 c.c. of boiling water are introduced into a flask of about 200 c.c. capacity fitted with rubber cork, through which pass two tubes. One of these leads into the lower end of a graduated tube of 150 c.c. capacity and the other is used to introduce liquid into the flask. Both tubes have rubber connexions which can be closed by means of pinch-

Nitro-cellulose

cocks. Air is expelled from the flask and tubes by boiling the water in it energetically for some time, and the pinchcocks are closed. Then the graduated tube is placed in position: 20 c.c. of hydrochloric acid and 20 c.c. of strong ferrous chloride solution are boiled up in a test-tube, and then the contents are drawn into the flask, care being taken not to admit any air. A little boiling water is added to wash out the test-tube, the admission tube is closed by means of its pinchcock, the contents of the flask are gently boiled, and the other tube leading to the measuring tube is opened. The gas comes off and passes into the measuring tube, which has been filled with strong sodium hydroxide solution and stands in a bath of the same liquid. The evolution lasts about fifteen minutes. Some more boiling water is then run into the flask to wash down any particles of unattacked nitro cellulose and the contents are then boiled again, this procedure being continued until there is no further evolution of gas. The orifice of the graduated tube is then covered with the thumb or finger protected with a rubber finger-stall, and removed to a large cylinder containing water, where it is allowed to cool. The tube is adjusted so that the water is at the same level inside and out, the volume of nitric oxide is then read, corrected for temperature and pressure and calculated to percentage of nitrogen.

In both the Lunge and the Schultze-Tiemann methods the nitrogen is measured as nitric oxide, NO. According to theory and the actual measurements of Leduc respectively 1 c.c. measured at 0° and 760 mm. is equal to:

Theory .	·0062707 g. N.	log. . . .	$\bar{2}$·79732	reciprocal . . 1·5947
Leduc .	·0062764		$\bar{2}$·79772	1·5932

Nitron Method. The nitro-cellulose is saponified by boiling with strong caustic soda, to which some hydrogen peroxide is added to prevent reduction. The solution is then diluted, acidified with sulphuric acid, and the nitric acid is precipitated with acetate of "nitron" (diphenylendianilodihydrotriazole).[1]

Concerning the determinatoin of nitrogen *see also* A. Koehler, M. Marqueyrol and H. Loriette, *Ann. Chim. Anal.*, 1914, p. 129; E. G. Beckett, *J. Soc. Chem. Ind.*, 1914, p. 628.

Solubility of nitro-cellulose.

All nitro-celluloses are soluble in acetone, ethyl-acetate, amyl-acetate, and some other organic solvents.[2] They are all insoluble in water and benzene, and all but the very low nitrated products are insoluble in either pure ether or alcohol except at very low temperatures, although commercial nitro-celluloses give up a small amount of fatty matter to ether, and resinous matter and decomposition products to alcohol. It should, however, be noted that commercial ethers usually contain a small proportion of alcohol, and if an ether of this kind be used, some of the nitro cellulose will be dissolved. The specific gravity of ether used for extracting fatty matter and nitro-glycerine from nitro-cellulose should not exceed 0·720.

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[1] Busch and Schneider, S.S., 1906, p. 232.

[2] *See also* Chapter XXIV.

The different nitro-celluloses are characterized by different degrees of solubility in a mixture of ether and alcohol. The highest nitrated products are practically insoluble in the mixed solvents. Gun-cottons containing 13 per cent. of nitrogen give up about 8 or 10 per cent., and as the percentage of nitrogen further falls, the solubility rapidly increases until with nitro-cottons containing about 12·3 per cent. solubility is practically complete. The degree of solubility is not conditioned solely by the percentage of nitrogen, however, but also depends upon the proportions of nitric and sulphuric acid used in nitration, and other details of preparation.[1]

Solubility determination.

The solubility of a gun-cotton in ether-alcohol depends to a certain extent upon the composition of the solvent used and the other conditions. It is, therefore, necessary to describe the exact method of carrying out the test. For testing the gun-cotton used in the manufacture of cordite the English War Department lay down the following rules:

50 grains (= 3·3 g.) of the air-dry gun-cotton are weighed out and transferred to a stoppered graduated cylinder of 200 c.c. capacity. A mixture is made of two volumes of ether to one of alcohol, 60 over proof, and 150 c.c. are poured on to the gun-cotton and occasionally agitated with it for about six hours at 15·5° and then allowed to settle. Seventy-five c.c. of the clear liquid are then transferred to a small weighed flask, the greater part of the ether and alcohol is distilled off, and the remainder is driven off by heating in a drying oven the temperature of which is not more than 49° (120° F.), the drying being continued until the weight is constant. The quantity of soluble matter must not be greater than 12 per cent.

This method cannot fail to give somewhat high results, as the whole of the solvents cannot be driven off in the manner prescribed. This, however, is not a matter of importance as the results are only intended to be comparative. A more serious objection to the test is that the results depend very largely upon the nature of the ether used, and no directions are given for selecting it. Methylated ether contains considerable proportions of ethyl-methyl ether and dimethyl ether, which have considerably greater solvent action upon gun-cotton than diethyl ether; and it also contains alcohol and water in various proportions. Constant results can only be obtained, therefore, if each supply of ether is tested upon a standard sample of gun-cotton. But even if two ethers give the same result with one sample of gun-cotton, they will not necessarily give the same result with another, which has been made by a different process.

The English official method given above is intended principally for nitro-celluloses, which are only slightly soluble in ethyl-alcohol; with those that are almost entirely soluble it is better to weigh the undissolved residue instead of the dissolved matter. For the soluble nitro-cellulose used for the manu-

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[1] *See* Chap. X, and Chap. XXIV.

facture of the United States nitro-cellulose powder the official method is as follows:

1 g. of the finely divided dry sample is treated with frequent stirring in a covered beaker or other suitable vessel with 350 c.c. of a mixture of pure ethyl alcohol and pure ethyl ether, the specific gravity of the mixture to be from 0·748 to 0·750 at 20°. The vessel is kept covered to prevent loss by evaporation. The residue is allowed to settle and the supernatant liquid siphoned off. The extraction with ether-alcohol solution is repeated twice: the insoluble residue is poured into a tared Gooch crucible having a thin asbestos filter, and well washed with ether alcohol. The residue is then partially dried at 80°, and the drying completed by exposure to a temperature of 100° till the weight is constant. The percentage of insoluble matter subtracted from 100 gives the per cent. of soluble nitro-cellulose, which must be at least 95 per cent. If "soluble nitro-cellulose" is to be determined in a nitro-cellulose containing considerably less than 95 per cent., the determination is made on 0·5 or less.

In Germany the following method is used: 2 g. of the fine sifted and well dried nitro-cellulose are placed in a 500 c.c. stoppered cylinder, 215 c.c. of alcohol (specific gravity 0·816 at 15°) are poured on, 285 c.c. of ether (specific gravity 0·720) are then added, the cylinder is shaken frequently for five hours and allowed to settle. Of the clear liquid, 250 c.c. are withdrawn, about 10 c.c. of water are added, and the mixture is evaporated to dryness. The residue is dried for half an hour at 80° and weighed.[1] The object of adding the alcohol first is to prevent the formation of a gelatinous mass.

The following method is given by H. C. Mallinson,[2] who claims that it gives reliable results in a short time: In a graduated cylinder are placed 200 c.c. of ether-alcohol and 5 grammes of the nitro-cotton, or 2 grammes if the solubility be 25 per cent. or more. This is shaken in a machine for one hour at six revolutions per minute. It is allowed to settle and 50 c.c. are drawn off into a porcelain dish. Then 500 c.c. of warm water (75 to 80° C.) are poured in slowly down the inside of the dish. This completely precipitates the dissolved nitro-cotton as a floating disc, which is freed from solvent by immersing it with a glass rod. If the nitro-cellulose be in one mass, it is now pressed between filter papers, then moistened with alcohol and pressed again and dried for twenty minutes at 70° and weighed. If not coherent, the nitro-cellulose is filtered off on a tared filter, washed with alcohol, dried and weighed. The results are consistent, but somewhat lower than those given by the British official method.

For methods used in France *see* *P. et S.*, 8, i., 135; 6, ii., 16; *Post et Neumann*, 2me ed., 1912. Tome III., Fasc. 1., p. 349.

The matter insoluble in acetone consists mostly of unnitrated or very

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[1] Kast, *Spreng- und Zündstoffe*, p. 930.

[2] *J. Ind. Eng. Chem.*, 1916, p. 401.

Nitro-cellulose

Matter insoluble in acetone.

imperfectly nitrated fibres. To determine it, 2 g. are treated with about 150 c.c. of acetone for six or eight hours with occasional shaking. It is then allowed to stand overnight and the clear liquid is carefully decanted off. The residue is washed several times by decantation with acetone, then transferred to a tared filter, washed again, dried in the water-bath, and weighed.

Unnitrated fibre in nitro-cellulose.

Unnitrated fibre is sometimes estimated by repeated treatment with sodium sulphide solution, which attacks the nitro-celluloses, but leaves the unnitrated cellulose unaffected. Lunge and Weintraub, however, found the method unsatisfactory, and recommend instead the use of sodium ethylate, which acts in a somewhat similar manner.[1] The method is specially useful in the case of products which contain a considerable proportion of matter insoluble in acetone.

In 100 c.c. of ordinary alcohol dissolve 3 g. of sodium, and if the liquid is not quite clear, filter. Add 100 c.c. of acetone, and set aside 50 c.c. of the mixture. Into the remaining 150 c.c. introduce about 5 g. of the nitro-cellulose. The action is hastened by warming on a water-bath to 40° or 50° with occasional agitation. In twenty or thirty minutes the action is complete; the brownish-red liquid is allowed to settle, and decanted through a small filter-paper, and the precipitate is washed by decantation with alcohol to remove any condensation products of acetone. The brown solid is then removed by treatment with water, and the residue is washed, first with hot water, and then with water containing a little hydrochloric acid. If the amount of unnitrated cellulose is considerable, or if a high degree of accuracy is not desired, this first treatment may suffice. The cellulose obtained evolves no gas in the nitrometer, but gives a strong reaction with diphenylamine, showing that traces of nitro-cellulose are still present. It may, therefore, be desirable to repeat the extraction. For this purpose the residue is first washed with alcohol to displace the water, and is then washed off the filter with the 50 c.c. of the acetone ethylate solution set aside as above. The remainder of the above treatment is then repeated and finally the cellulose is washed with water, dried at 100°, and weighed. It now only gives a slight blue coloration with diphenylamine. The cellulose residue should only have a very slight brown colour, which may be removed by treatment with bleaching solution. A good nitro-cellulose contains hardly any unnitrated fibre.[2]

Free acid and alkali.

Free acid and alkali may be determined in nitro-cellulose by extracting the finely divided material with hot water, filtering, and titrating in the usual way. Very thorough washing is necessary, as the material has the property of absorbing considerable quantities of acid and alkali. When testing for minute traces it is necessary carefully to examine the water and other materials used.

Nitro-cellulose usually contains more or less calcium carbonate, which has

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[1] *Ang.*, 1899, p. 473.

[2] *See also* Kast, *Spreng- und Zündstoffe*, p. 929.

either been added intentionally or has been precipitated from the water used for boiling the material during the stabilization. To determine this, digest a known weight of the sample with a known volume of cold diluted standard hydrochloric acid, filter, wash thoroughly and titrate, using methyl orange or other suitable indicator.

Discoloration. Really pure nitro cellulose when gelatinized is quite white, but it has often a slight brown tint due to oxide of iron precipitated in the fibres during manufacture. When stored in a wet condition, it frequently becomes quite black, especially on the surface, in consequence of bacterial action. The bacteria, however, attack mostly the paper or other organic material in contact with the nitro-cellulose. This discoloured nitro-cellulose generally gives a low heat test.

Ash. The gun-cotton is mixed with paraffin-wax and paraffin oil is a large crucible, and the mixture is set alight, a small flame being kept going underneath. As it burns away, more wax is added from time to time. The flame must not be allowed to come in contact with the gun cotton itself until it has been broken down by the heat. Finally the crucible is ignited to destroy all organic matter, cooled and weighed.

In America the ash is determined by placing 1 gramme in a platinum capsule with 3 c.c. of nitric acid, evaporating down and then igniting. In France it is ascertained by dissolving in acetone and castor oil, burning off and igniting.[1]

Microscopic examination. For microscopic examination it is best to embed the nitro-cellulose in Canada balsam or moisten it with 50 per cent. alcohol. In polarized light the fibres appear of various colours depending upon the degree of nitration and conditions of manufacture, and can readily be distinguished from unnitrated cellulose and foreign matter. For details of this and other optical properties, *see* Mosenthal, *J. Soc. Chem. Ind.*, 1907, p. 1; also Ambronn, *Kolloid-Zeitschrift*, 1913, p. 200.

Sulphuric esters. It was shown by Cross, Bevan, and Jenks[2] that during the process of nitrating cotton a small proportion of mixed sulphuric nitric esters of cellulose is formed, and it was demonstrated by Hake and Lewis[3] that these bodies are considerably less stable than the pure nitric esters.

The method of determination adopted by Hake and Lewis was to saponify with caustic soda, add sodium carbonate, evaporate to dryness, ignite, dissolve in water, acidify with hydrochloric acid and precipitate with barium chloride. The method has been criticized adversely by Kullgren,[4] who found that it gave low and erratic results: it is in fact impossible to precipitate barium sulphate in the presence of large quantities of alkali salts without incurring

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[1] Buisson, *Problème des Poudres*, pp. 56 and 33.

[2] *Ber.*, 1901, p. 2496.

[3] *J. Soc. Chem. Ind.*, 1905, vol. 24, pp. 374 and 914; 1906, vol. 25, p. 624.

[4] *S.S.*, 1912, p. 89.

many large sources of error,[1] and here the quantity is at least eight times that of the nitro-cellulose and several thousand times that of the sulphuric acid.

Kullgren decomposes the nitro-cellulose with hydrochloric acid, evaporates to dryness, and then burns the material in a current of oxygen and absorbs the oxides of sulphur on quartz grains coated with soda. He then dissolves the salts off the quartz, adds a little sodium peroxide to complete the oxidation, and precipitates with barium chloride. The results he obtained, about 1·6 per cent. of sulphuric acid, are so very high that doubt is thrown on the method.

There is no reason why the method, which has been used with success for the determination of sulphur in pyrites and in vulcanized rubber goods, should not be used here. The nitro-cellulose is heated in a covered beaker with concentrated nitric acid (specific gravity 1·5), one or two small crystals of potassium chlorate are added from time to time, the liquid is evaporated to dryness, the residue moistened with hydrochloric acid, which is evaporated off again, then moistened with a little hydrochloric acid, dissolved in dilute hot water and precipitated with a small quantity of a dilute solution of barium chloride. A blank test should be carried out with the reagents, and the result corrected accordingly.

Viscosity of solutions of nitro-cellulose.

In the case of collodion cotton, that is to be used in the manufacture of blasting gelatine, it is necessary that the solution in nitro glycerine be a stiff semi-solid. Different samples of collodion cotton differ very much as regards this property. A nitro-cellulose which produces a very stiff colloid when a little of it is dissolved in nitro-glycerine, will also yield a very viscous solution when it is dissolved in some other solvent, such as ether alcohol or acetone. It is therefore usual to determine the viscosity of a solution of convenient strength, 1 or 2 per cent., in one of these solvents.

The viscosity of a liquid is generally determined by measuring the time that a certain volume of the liquid takes to flow through an orifice. If r be the radius of the orifice and l its length, p the difference of pressure at its two ends, and V the volume that flows through in time t, then the viscosity η measured in absolute units (centimetre gramme-second) is given by the equation :

$$\eta = \frac{\pi p r^4 t}{8 l V}$$

In order to obtain reliable results it is necessary that l be large compared with r, that is to say, a narrow tube should be used. The absolute viscosities of solutions of nitro-celluloses of different concentrations have been measured by Baker.[2] The viscosity increases very rapidly with concentration, and even the logarithm of η rises greatly as the concentration is increased.

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[1] *See* Allen and Johnston, *J. Amer. Chem. Soc.*, 1910, p. 588.

[2] *Trans. Chem. Soc.*, 1913, p. 1653.

Viscosity of solutions of nitro-cellulose.

For the commercial testing of oils it is usual to use a standard instrument, such as the viscometers of Redwood or Engler, in which the time of flow through an orifice is taken under conditions that are accurately defined, and this time is compared with that taken by a standard liquid, such as rape-oil or water. The Engler viscometer has been used also for the examination of solutions of collodion cottons. The orifices of these viscometers are short, and consequently the results are not always converted readily into absolute viscosities.[1] In some factories use is made of a rough instrument consisting merely of a 50 c.c. pipette with a mark below the bulb as well as one above it. The time is measured that is required for the level of liquid to fall from the upper mark to the lower one, and this time is divided by the time taken by pure acetone or other standard liquid.

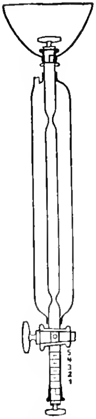

FIG. 155.
Cochius Viscometer

The temperature of the liquid must always be regulated carefully, as variations affect the results considerably. The solutions must be allowed to stand a day or more before being tested, in order that solution may be complete, and all undissolved particles may settle out. If a particle of undissolved or partially dissolved cotton clog the orifice, the time found will be too long, of course. In order to overcome this difficulty Cochius has devised an instrument in which the relative viscosity is ascertained by measuring the time that a bubble of air of known size takes to ascend through a certain column of the liquid. The instrument is shown in Fig. 155. The inner tube is filled with the liquid under examination, and the size of the air bubble is regulated in the lower graduated portion. By turning the cock through 90° the bubble is admitted to the other part of the tube; the time is measured from the instant the bubble leaves the lower constriction to the instant it reaches the upper one. The tube is surrounded by a water jacket to facilitate the regulation of the temperature.

The viscosity of a solution does not alter much with time, provided that it be not exposed to light or heat.[2] A high viscosity is considered to indicate that the molecular complexity of the nitro-cotton is great. It has been found by Piest[3] that the addition of 10 per cent. of a solution of a nitro cotton, that does not give viscous solutions, to a viscous one, causes a very great fall in the viscosity, whereas the addition of 10 per cent. of a more dilute solution

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[1] For the conversion of viscometer readings into true viscosity, *see* C. A. Saville and A. W. Cox, *J. Soc. Chem. Ind.*, 1916, p. 151; *also* P. C. McIlhiney, *J. Ind. Eng. Chem.*, 1916, p. 433.

[2] *See* R. Fric, *Compt. rend.*, 1912, p. 31.

[3] *Ang.*, 1913, p. 24.

of the sample of high viscosity causes a comparatively small fall. In the latter case the viscosity of the mixed solution is about that calculated from the viscosity of the constituent solutions. This phenomenon is consistent with the theory that the liquid really dissolves in the nitro-cotton rather than the nitro-cotton in the liquid.

For making blasting gelatine and other similar high explosives the viscosity should be high, as already stated. For artificial silk, on the other hand, it should be low; and for some other purposes, such as the preparation of collodion solution for dipping incandescent gas-mantles, an intermediate value is required.[1]

Fineness. It is often of importance to ascertain the relative fineness to which nitro-cotton has been pulped. This can be done roughly by examining the material under a lens, but the following test is more satisfactory, as it enables a definite figure to be assigned: 10 g. of the nitro-cotton are placed in a 200 c.c. graduated cylinder, water is added to the 200 c.c. mark, and the cylinder is shaken for three minutes. It is allowed to settle for half an hour, and the volume occupied by the pulp is read off. The finer the pulp the smaller is the volume.

NITRO-COMPOUNDS

Melting point. If it can be separated in a state of purity an aromatic nitro-compound can be identified by taking its melting-point. The following are the melting points of a few of those most used in explosives:

Substance	Melting-point
m-dinitro-benzene	90°
2 : 4-dinitro-toluene	70
α-trinitro-toluene (trotyl)	81°
α-nitro-naphthalene	59°
Tetryl	129–130
2 : 4-dinitro-phenol	114°
Picric acid	122°
Trinitro-cresol	105–106°
Trinitro-anisole	64–65°

The higher nitro naphthalenes are usually complex mixtures from which it is not easy to separate the constituents.

In some cases the substance can be recognized by a characteristic colour reaction. Mono-nitro-naphthalene, for instance, gives a brilliant red coloration when heated with strong sulphuric acid. Dinitro-naphthalene, if dissolved in strong sulphuric acid and reduced with zinc and thrown into water, gives a fine reddish violet coloration. The following colours are obtained when small quantities are dissolved in 2 or 3 c.c. of acetone or methyl alcohol and a few drops of 10 per cent. caustic soda or potash are added:[2]

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[1] For the estimation of the relative viscosities of very concentrated solutions of nitro-cellulose, *see* T. Chandelon, *Bull. Soc. Chim. Belg.*, 1914, p. 24.

[2] *U.S. Bureau of Mines Bulletin*, No. 51, p. 17.

Nitro-benzene	no effect
Dinitro-benzene	purple rose, turning to deep claret
Trinitro-benzene	rich purple brown
Nitro-toluene (*o*)	no effect
,, (*m*)	slight yellow
,, (*p*)	no effect
Dinitro-toluene	gradual evolution of azure blue on standing
Trinitro-toluene	deep wine-red brown
Nitro-naphthalene	no effect
Dinitro-naphthalene	reddish yellow
Trinitro-naphthalene	bright scarlet
Tetranitro-naphthalene	reddish yellow
Picric acid	precipitate of crystals of potassium picrate (orange)

In a mixture the colour produced by one substance may obscure that of others. The wine-red coloration produced by trinitro-toluene, for instance, may prevent the identification of other compounds.

The determination of the melting-point is also the most usual method of ascertaining the degree of purity of such compounds. To carry it out a small quantity of the substance is placed in a piece of thin walled capillary tube, made by drawing out a test tube in the blow-pipe flame. This tube is attached to a thermometer so that the substance is level with the centre of the bulb. The thermometer is then immersed in a beaker of clear liquid, water if the melting-point be below 100°, otherwise sulphuric acid. The temperature of the liquid is then gradually raised, the liquid being stirred continuously. The temperature is then observed at which the substance in the capillary tube becomes liquid. If it be pure, the melting-point is very sharp. If any part of the mercury column of the thermometer be not immersed in the liquid, and accurate results be required, the usual correction must be made.

Impurities.

Certain impurities can also be tested for directly. The ash and the amount insoluble in a suitable solvent may be determined, as also the volatile matter. The insoluble matter should be examined to ascertain whether it is of a gritty character. The nitro-compounds generally used in explosives are much more stable than nitro-cellulose or nitro-glycerine. They should give a heat test of over sixty minutes at 80° or 90°. They are sometimes tested by heating *in vacuo* at a temperature of 130° or more, and measuring the gas evolved in a fixed time.

They may be tested in some cases by a determination of the nitrogen, or, if the percentage of nitrogen be known, this test may be used to ascertain the quantity of the compound present.

Nitrogen determination.

The nitrogen of nitro- and nitroso-compounds is not given off in the nitrometer nor in the Schultze-Tiemann process. Consequently these methods are not available. The total nitrogen in any organic compound can be determined by Dumas' method, which consists in igniting it with copper oxide an atmosphere of carbon dioxide and passing the gases evolved over heated copper oxide or lead chromate and metallic copper; the last portions of gas are displaced with carbon dioxide, and collected over caustic soda solution, which absorbs the carbon dioxide. Some methyl derivatives give off also methane in this test and consequently yield high results. These should be mixed with cuprous or cupric chloride, which cause the methane to be burnt.[1]

Kjeldahl method.

In most nitro-compounds the nitrogen can be determined satisfactorily by the Kjeldahl method as modified by Gunning and Jodlbauer. For this weigh out about 0·5 gramme and place it in a long-necked Kjeldahl flask. Pour over it rapidly 30 c.c. of strong sulphuric acid containing 2 grammes of salicylic acid. Dissolve the nitro-compound by rotating the flask and warming it, if necessary, in a water-bath. After cooling, add 2 grammes of zinc dust, a little at a time, continually rotating the flask to prevent local heating. Agitate the flask occasionally for an hour or two and leave it over night. Next day heat it in a water-bath for an hour at 70°, and then over a small flame until all visible action is over. Then cool slightly and add about a gramme of mercury or mercuric oxide, boil gently for one or one and a half hours. After cooling add 7·5 grammes of potassium sulphate and 10 c.c. more sulphuric acid, and boil for a further one or one and a half hours. Cool the flask and add 250 c.c. distilled water to dissolve the cake formed, then add 25 c.c. of potassium sulphide solution (8 per cent.), 1 gramme of granulated zinc and 85 to 90 c.c. of strong caustic soda solution (750 grammes to a litre of distilled water), or enough to make the liquid strongly alkaline. The ammonia is then distilled off and titrated. This method gives good results with the various nitro-toluenes, picric acid, nitro- and dinitro-benzene and -aniline and nitro-naphthalene, as also with potassium and ammonium nitrate and urea nitrate, but W. C. Cope[2] found that it gives low results with tetranitro-aniline, tetra-nitro-methyl-aniline (tetryl) and dinitro-naphthalene.

It is stated by A. Eckert[3] that aromatic nitro-compounds can be reduced by warming 0·2 to 0·5 gramme with 15 to 20 c.c. of 30 to 40 per cent. oleum, and 0·4 gramme sulphur on a water-bath for an hour. The liquid is then diluted and distilled with alkali as in the Kjeldahl method. This process gives low results with aliphatic nitro-compounds and inorganic nitrates, but was satisfactory with nitro-benzene, brom-nitrobenzene and a large number of other aromatic nitro-compounds.

Decomposition flask method.

It has been found by E. Berl and A. W. Jurissen that if a nitro-compound be oxidized with a mixture of sulphuric and chromic acids, the nitrogen is brought into such a form that on subsequently shaking with mercury it is all evolved as nitric oxide. Hence they have evolved a method of determining

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[1] P. Haas, *Trans. Chem. Soc.*, 1906, p. 570.

[2] *J. Ind. Eng. Chem.*, 1916, p. 592.

[3] *Monatsh*, 1913, 24, p. 1957.

Nitro-compounds

the nitrogen by means of their "decomposition flask."[1] This is a thick round-bottomed flask of 250 to 300 c.c. capacity with a ground in stopper provided with a dropping funnel and a tube of narrow bore carrying a three-way cock.[2] All the joints are well ground in. The substance under analysis is placed in the bottom of the flask, taking care not to let it hang on the walls. One orifice of the three-way cock is connected with a vacuum pump, and the other with a generator of pure carbon dioxide. The flask is evacuated and filled with carbon dioxide several times and finally evacuated. Then 40 c.c. of strong sulphuric acid are drawn in through the dropping funnel, and the narrow tube and cock of the funnel are filled with a few drops of 30 per cent. sulphuric acid. Some 4 or 5 c.c. of a saturated solution of chromic acid are then added, taking care not to allow any air to enter the flask. By carefully warming and gently agitating the flask the organic substance is oxidized to carbon dioxide together with a little carbon monoxide. Solution is complete in a few minutes. The flask is then cooled and the chromic acid in the entrance tube and cock is displaced with dilute sulphuric acid. After which 2 or 3 c.c. of mercury are added and the flask is shaken vigorously. The chromic acid thus is reduced to chromium sulphate and the nitrogen to nitric oxide. The vacuum is then destroyed by running in boiled (air-free) solution of sodium sulphate. The flask is connected with a nitrometer and the gas is displaced into it by running in more sodium sulphate solution. This gas consists of carbon dioxide and monoxide and nitric oxide. The carbon dioxide is absorbed by running in from the cup of the nitrometer a little caustic potash solution, which must not be of more than 20 or 30 per cent. strength, else it will convert some of the nitric oxide into nitrous oxide. If there be much carbon dioxide it may be necessary to pass part of the gas first into the nitrometer, absorb the greater part of the carbon dioxide, and then pass in more gas. When all has been passed in, and all the carbon dioxide has been absorbed, the volume is read. Then it is passed into an absorption pipette where it is treated with a saturated solution of ferrous sulphate to absorb the nitric oxide. The residue, consisting mainly of carbon monoxide, is then passed back into the nitrometer and measured, and its volume is deducted from the former volume. The volume must be corrected, not only for temperature and pressure, but also for the vapour of the caustic potash solution. The following are the vapour pressures of a solution of 30 parts KOH in 100 parts water:

10°	7·3 mm.
15°	10·1 mm.
20°	13·9 mm.
25°	18·9 mm.

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[1] *Ang.*, 1910, p. 241; *S.S.*, 1910, p. 61; Lunge-Berl, *Chemischtechnische Untersuchungs-Methoden*, 6th ed., vol. 3, p. 123.

[2] These flasks may be obtained from Drs. Bender and Hobein, Zurich.

Nitro-compounds

This method has given satisfactory results with trinitro-toluene, dinitro-toluene, picric acid, nitro naphthalene, nitro dimethyl aniline and aurantia (the ammonium salt of hexanitro-diphenylamine). In the last two cases it gives the nitrogen in the nitro-groups only. The authors also recommend the use of this process for gelatinized nitro-cellulose, which dissolves much more rapidly in the mixture of sulphuric and chromic acids than in sulphuric alone. Also, if a smokeless powder contain diphenylamine, mineral jelly or other substance capable of absorbing oxides of nitrogen, the ordinary method in the Lunge nitrometer gives low results.

For the analysis of mineral nitrates, ungelatinized nitro-cotton and other nitric esters, that are easily dissolved, chromic acid is not needed, and the nitric oxide formed has only to be transferred to a graduated tube and measured in the usual way.

Stannou chloride method.

The "nitro"-nitrogen can also be determined in many cases by titration with stannous chloride solution in the presence of hydrochloric acid, the nitro-compound being reduced to the corresponding amine:

$$R.NO_2 + 3SnCl_2 + 6HCl = R.NH_2 + 3SnCl_4 + 2H_2O$$

The stannous chloride solution is made by dissolving 150 grammes of tin in concentrated hydrochloric acid. The clear liquid is decanted, mixed with 50 c.c. of concentrated hydrochloric acid and diluted to 1 litre. Its strength is determined by titrating with standard iodine solution after adding sodium carbonate. Of the nitro-compound about 0·2 gramme is weighed out, placed in a 100 c.c. stoppered flask with 10 c.c. of the stannous chloride solution and warmed for thirty minutes. When cool it is made up to the mark with water, and 10 c.c. are transferred to a beaker. A little water is added and then sodium carbonate solution until the precipitate which forms at first is wholly dissolved. It is then titrated with decinormal iodine solution using starch as an indicator. The method does not work with nitro-naphthalene or picric acid.[1]

Titanium chloride method.

Another simple titration process is that with a standard solution of titanium chloride.[2] It can be used for nitro-, nitroso-, and azo compounds. To prepare the solution, commercial titanium chloride is boiled briskly with an equal volume of strong hydrochloric acid to remove traces of hydrogen sulphide, and then diluted to twenty times its original volume with water free from oxygen. In the absence of air it retains its strength for a considerable time. Its titre is determined by titrating a known volume with a standard solution of iron alum, the end point being ascertained by testing a drop with potassium thiocyanate. The nitro-compound to be tested is treated in an atmosphere

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[1] *See* H. Limpricht, *Ber.*, vol. 11, p. 35; Spindler, *Annalen*, 224, p. 288; Jenssen *J. pr. Chem.*, 78, p. 193; S. W. Young, *J. Amer. Chem. Soc.*, 1897, p. 812; P. Altmann, *J. pr. Chem.*, vol. 63, 1901, p. 370.

[2] Knecht, *J. Soc. Dyers*, 1903, p. 169; 1905, pp. 111, 292.

of carbon dioxide with a known excess of the titanium solution and the excess is titrated with the alum solution.

When azo-dyestuffs are titrated, it is not necessasy to use the drop reaction : they can be titrated directly, the colour change indicating the end point. H. Salvaterra[1] makes use of this property in testing nitro-compounds. After treating the substance with a known excess of titanium solution, he adds an excess of a standard solution of methylene blue, heats to boiling and titrates back with the titanium solution. There is a sharp change from green to yellow. This method gives good results with picric acid. $TiCl_3 = FeCl_3$: $6TiCl_3 = NO_2$: $4TiCl_3 = NO = RN_2R$.

NITRO-GLYCERINE

$C_3H_5N_3O_9 = C_3H_5(NO_3)_3$. Molecular weight 227·1

(*See also* Chapter XVI)

Properties. Nitro-glycerine (glycerol trinitrate) is a heavy oily liquid, which when pure is colourless, but the commercial product is pale yellow. The specific gravity of the liquid is 1·6144 at 4°, 1·6009 at 15° and 1·5910 at 25°.[2] On freezing it contracts and the specific gravity of the solid is 1·735. It is not hygroscopic and is almost insoluble in water, 1 gramme requiring 800 c.c. for solution. It is also practically insoluble in glycerine, turpentine, petroleum spirit and other mineral oils, but is readily soluble in ether, ethyl acetate, acetone, ethyl and methyl alcohol, chloroform, glacial acetic acid, amyl alcohol, benzene, toluene, nitro-benzene, phenol, olive oil and sulphuric acid. It dissolves less readily in carbon bisulphide, nitric acid, and hydrochloric acid.[3] It dissolves nitro-aromatic compounds and takes up a small quantity of resin, etc., from wood meal, but it does not dissolve oils, mineral jelly or sulphur.[4] At moderately low temperatures nitro-glycerine is liable to solidify. The melting-point of the pure substance is 13·3° :[5] it crystallizes in the rhombic system.[6] There is also a labile solid modification, which melts at 2·8° (Kast) or 2·0° (Hibbert) and forms crystals belonging to the triclinic system. In the changes of state thus involved the following quantities of heat are evolved :[7]

	Calories per g.	Calories per mol.
Fluid to labile	5·2	1·18
Labile to stable	28·0	6·36
Fluid to stable.	33·2	7·54

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[1] *Chem. Zeit.*, 38, 1914, p. 90.

[2] Perkin, *Trans. Chem. Soc.*, 1889, p. 326.

[3] *See* Elliott, *School of Mines Quarterly*, vol. 4, p. 15.

[4] *Bureau of Mines Bulletin*, No. 96, p. 45.

[5] S. Naukhoff, *S.S.*, 1911, p. 124 ; *see also* Kast, *S.S.*, 1906, p. 225 ; Hibbert, *Eighth Inter. Cong. Appl. Chem.*, 1912, vol. 4, p. 37.

[6] For measurements of crystals, *see* S. Naukhoff, *loc cit.*

[7] H. Hibbert and G. P. Fuller, *J. Amer. Chem. Soc.*, 1913, p. 978.

The melting-point of the commercial product is often some degrees lower than these figures in consequence of the presence of dinitro-glycerine and other substances. (*See also* Chapter XVII.)

Nitro-glycerine is slightly volatile at the ordinary temperature; the vapour pressures at various temperatures were determined by G. Peace and myself[1] by passing known volumes of air over nitro-glycerine or cordite, condensing the nitro-glycerine vaporized and weighing it:

Temperature °C.	Vapour Pressure mm. of mercury
20	0·00025
30	0·00083
40	0·0024
50	0·0072
60	0·019
70	0·043
80	0·098
90	0·23
93·3	0·29

The vapour pressure at 25° has also been calculated by D. Chiaraviglio and O. M. Corbino from the rate of distillation in a high vacuum.[2] They thus arrive at the volume 0·00012, which may be considered a fair agreement considering the uncertainty of the latter method. If distilled with steam Haeussermann[3] found that 1 litre of water carried over 8 grammes of nitro-glycerine: from this observation the vapour pressure is calculated to be 0·48 mm. at 100°, which is in excellent agreement with the above table. Under a pressure of 15 mm. it evaporates rapidly at a temperature of 160° without actually boiling.[4] Robertson found that at 125° decomposition proceeds at such a rate that 2·5 g. give off 1·6 mg. of nitrogen in the form of nitric peroxide, and that this rate is doubled for every rise of 5°.[5] At 145° the evolution of decomposition products is so rapid that the liquid appears to boil at atmospheric pressure: the gaseous products of decomposition carry over with them nitro glycerine, nitric acid, water, and other liquid products, which can be condensed.[6] At about 218° nitro-glycerine explodes.

Physiological action.

Nitro-glycerine has a very powerful physiological effect. Merely handling it or entering a house containing it will often give a violent headache to any one not accustomed to it. The best antidote is strong coffee. It is used in medicine either in the form of a 1 per cent. solution in alcohol, "liquor trinitrini,"

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[1] *Trans. Chem. Soc.*, 1916, p. 298.

[2] *Atti R. Accad. Lincei*, 1914, p. 37; *Gazzetta*, 1916, p. 368.

[3] R. Escales, *Nitro-glycerin und Dynamit*, p. 133.

[4] Lobry de Bruyn, *Rec. Trav. Chim.*, 1895, p. 131.

[5] *Seventh Inter. Cong. Appl. Chem.*, 1909, iii B, p. 95.

[6] Snelling and Storm, *U.S. Bureau of Mines Technical Paper*, No. 12.

Nitro-glycerine

or mixed with chocolate in the form of tablets weighing 0·30 gramme each, and containing 0·5 mg. of nitro-glycerine; these are called "tabellæ trinitrini." The dose is 0·5 to 1 mg. of nitro-glycerine, but single doses of 0·32 gramme and daily doses of 1·3 gramme have been administered medicinally with safety.[1] It is administered to reduce arterial tension in cases of arterial degeneration and chronic Bright's disease, also to relieve difficulty in breathing in cases of asthma, etc. It is absorbed unaltered by the stomach, and is supposed to be converted into nitrite in the body. Its action resembles that of amyl nitrite, but is less rapid and is more prolonged.[2]

Detection. If some of the dry explosive (1 to 5 g.) is placed in a dish on a boiling water-bath, and the dish is covered over with a glass beaker or funnel, after an hour the glass will be found to be clouded with minute drops of nitro-glycerine, if any be present. The appearance is very characteristic, and quite distinct from that of the large drops of liquid which may be formed in consequence of the presence of water or organic solvents.

Nitro-glycerine can also be detected by extracting with ether, evaporating off the solvent, and examining the residue. If the residue is a viscous liquid readily soluble in 80 per cent. methyl alcohol, but insoluble in water, it is probably nitro-glycerine. Absorb some of it in filter-paper and set fire to it. It will burn quietly with a peculiar green flame.

Examination. Nitro-glycerine as such is not allowed to be transported out of the factory at which it is made, and for extra security it is usual to mix it as soon as possible with gun-cotton or some other material which renders it less sensitive. Consequently the examination of commercial nitro-glycerine is hardly ever carried out, except in the factory.

The percentage of *nitrogen* may be ascertained by weighing out 0·32 to 0·35 g. into a small beaker, dissolving it in sulphuric acid and introducing it into the Lunge nitrometer, as described above, under nitro-cellulose. The theoretical percentage is 18·53. The results obtained are often 0·1 to 0·2 per cent. lower than this. If the percentage of nitrogen is very low, it shows the presence of dinitro-glycerine or some other impurity.

To determine the alkalinity take 20 g., shake up with 50 c.c. of water, and titrate with decinormal sulphuric acid, using methyl orange as indicator. For nitro-glycerine used in the manufacture of cordite, it is specified that the alkalinity shall not exceed 0·005 per cent. calculated as sodium carbonate.

Moisture may be determined by weighing out about 5 g. into a small dish and allowing it to stand at the ordinary temperature over calcium chloride in a desiccator, which may be evacuated if preferred. It should not exceed 0·5 per cent.

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[1] *Brit. Med. Jour.*, 1905, Epitome ii, p. 52; W. H. Martindale, *Nature*, July 29, 1915, p. 591.

[2] *See also* Weinberg, *S.S.*, 1911, p. 427.

Stability Tests. The only test usually applied is the Abel heat test, *q.v.* Guttmann's test cannot be utilized with explosives containing nitro-glycerine.

Estimation of nitro-glycerine.

In consequence of the volatility of nitro-glycerine there is some difficulty in weighing it after extracting it by means of a solvent from a composite explosive. When possible it is therefore estimated by difference, but in many cases it is very desirable to estimate the nitro-glycerine directly. If it is known that no other substance is present, which will evolve nitrogen, or combine with nitric acid in the nitrometer, the percentage of nitro-glycerine can be deduced from a nitrogen determination on the explosive. Or if the amount of nitrogen due to other nitric esters or nitrates is known, it is still possible to calculate the percentage of nitro-glycerine. Almost the whole of the ether can be evaporated off from the ether extract of an explosive without incurring an appreciable loss of nitro-glycerine, provided it be done at a low temperature.[1] The beaker containing the ether solution is placed on a ground glass plate and covered with a bell jar having two tubulars through which pass glass tubes. A rapid current of air dried by means of sulphuric acid is made to enter through one of these tubes, and is delivered downwards about half an inch above the surface of the ether. The air current is regulated so that a marked dimple is made on the surface of the solution. The air and vapour pass out through the other tube, and may be led out of the laboratory window. The current of air should be passed for about six hours. The nitro-glycerine can then be estimated in the residue by means of the nitrometer.

Silberrad, Ablett, and Merryman [2] have worked out a method for the direct estimation of nitro-glycerine which is as follows: A weighed quantity of the ground cordite, or other explosive sufficient to yield 1·5 g. of nitro-glycerine, is placed in a thimble in the extractor A (Fig. 156) which is fitted up as shown. Eighty c.c. of absolute ether is poured into the flask and extraction is carried out in the usual manner. After the extraction is complete, the thimble containing the nitro-cellulose, etc., is washed with a little fresh ether, and removed from the extractor, a little ether being left in the latter. The absorption flasks C, containing 10 c.c. of $N/10$ acid, are now affixed and excess of sodium ethylate (about 50 c.c. of a solution prepared by dissolving 5 g. of sodium in 100 c.c. of absolute alcohol) is run into the flask little by little through the side tube D. About 10 c.c. of ethylate solution are also blown up through the stopcock E, into the extractor. The reaction takes place rapidly and is completed by warming on the water-bath for about six hours; its course may be followed by periodically drawing off small samples by means of the tap E, filtering them and examining them for nitro glycerine by means of diphenylamine in sulphuric acid. The ether is then distilled up into the extractor and run off by means of the tap, and the apparatus is cleansed

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[1] A. L. Hyde, *U.S. Bureau of Mines Bulletin*, No. 51, p. 40.

[2] *J. Soc. Chem. Ind.*, 1906, vol. 25, p. 628.

of vapour by blowing air through. The residue in the flask is dissolved in water and transferred to a 150 c.c. flask, the washings of the flask and extractor are added, and the volume of liquid is made up to the mark. Fifty c.c. of the solution are then transferred to the flask F, of the reduction apparatus (Fig. 157), 50 g. of a mixture of powdered zinc (2 parts) and reduced iron (1 part) are added together with 50 c.c. of 4 per cent. sodium hydroxide solution, 60 c.c. of N/10 acid being placed in the absorption flasks H. After the apparatus has stood in the cold for one hour, the contents of the flask F are boiled. After boiling for one hour a current of air is passed through for one and a half hours, boiling being still continued. For the last half-hour there should be no water in the condenser. The excess of standard acid is then titrated back. Each c.c. of N/10 acid corresponds to 0·007567 g. of nitro-glycerine. The experimental error does not exceed 1 per cent.

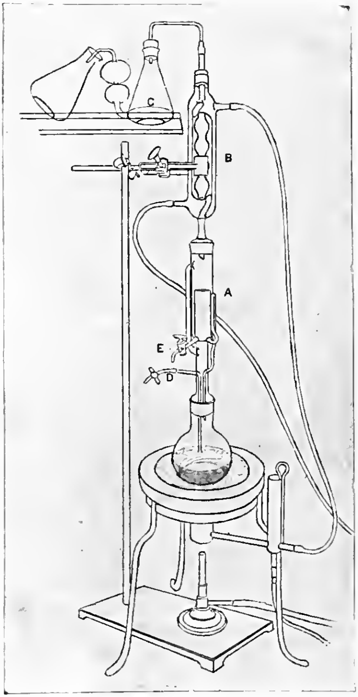

FIG. 156. Apparatus for the Determination of Nitro-glycerine

Separation from nitro-aromatic compounds.

Many blasting explosives contain nitro-glycerine together with a nitro-derivative of an aromatic hydrocarbon, etc. The separate estimation of these substances presents some difficulty, as they are soluble in practically all the same solvents, and nitro-glycerine is slightly volatile. If the mixture consist of nitro-glycerine and di- or tri-nitro-toluene, the nitro-glycerine can be determined by dissolving in sulphuric acid and shaking up in a nitrometer in the usual way. The di- or tri-nitro-toluene does not interfere with the reaction to an appreciable extent, but if mono-nitro-toluene be present, it is converted into dinitro-toluene, and the nitrometer reading is correspondingly low.[1] Similarly mono- and di-nitro-naphthalene are converted into the trinitro-

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[1] Storm, *Eighth Inter. Cong. Appl. Chem.*, 1912, vol. 4, p. 117.

derivative,[1] and nitro-benzene into dinitro-benzene. According to E. Küppers, nitro-glycerine can be estimated in admixture with nitro-compounds by determining the nitrogen by the Schultze-Tiemann method.[2] As the evolution of nitric oxide is very rapid from nitro-glycerine in this test, H. Pellet recommends that it be introduced into the reaction flask gradually after the reagents.[3] Hyde[4] has proposed to separate the nitro-glycerine from the nitro-derivatives by treatment with immiscible solvents, consisting of carbon bisulphide, on the one hand, and a mixture of 65 parts acetic acid and 35 parts water on the other. But the separation is very incomplete even after several extractions, and a large correction consequently has to be made.

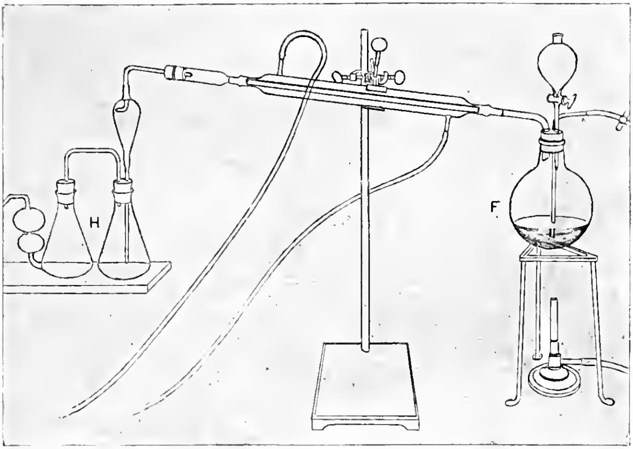

FIG. 157. Apparatus for the Determination of Nitro-glycerine

Estimation of small quantities.

For the estimation of small quantities, such as are used in medicine, Scoville recommends the colorimetric method with phenol disulphonic acid as used in water analysis.[5] An amount of the alcoholic solution of the substance equivalent to about 0·00065 g. (0·01 grain) of nitro-glycerine is allowed

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[1] *U.S. Bureau of Mines Bulletin*, No. 96, p. 44.

[2] *S.S.*, 1915, p. 146.

[3] *Ann. Chim. anal.*, 1911, p. 294.

[4] Storm, *Eighth Inter. Cong. Appl. Chem.*, 1912, vol. 4, p. 69. *See also J. Am. Chem. Soc.*, 1913, p. 1173; *Ang.*, 1914, vol. ii, p. 85.

[5] *Amer. J. Pharm.*, 1911, p. 359.

to evaporate spontaneously. If tablets are to be examined, five of them are powdered, shaken with 10 c.c. of alcohol for one or two hours, the solution filtered, and 2 c.c. of the filtrate are then treated as above. When dry, 2 c.c. of phenol disulphonic acid reagent are added, the mixture is well stirred, allowed to stand ten minutes, diluted with water, made slightly alkaline with potassium hydroxide, and diluted to 100 c.c. At the same time an approximately equivalent quantity of a solution containing 0·7215 g. of potassium nitrate per litre is measured out, evaporated down and treated in the same way, and the colorations, due to the formation of picric acid, are compared. 1·2 c.c. of the standard solution is equivalent to 0·01 grain nitro-glycerine.

Tetranitro-diglycerine. Tetranitro diglycerine, and other nitro-polyglycerines, are distinguished from nitro-glycerine by the fact that they are only slightly soluble in a 60 per cent. solution of acetic acid, which dissolves over 9 per cent. of nitro-glycerine. The proportion of tetranitro-diglycerine in a mixture with nitro-glycerine may be estimated by determining the nitrogen in the sample, after filtering, if necessary, to remove oils, etc. Or the molecular weight may be determined by the boiling-point method using ethyl acetate as solvent.[1] Tetranitro diglycerine has a molecular weight of 346 and contains 16·2 per cent. N, whereas the corresponding figures for nitro-glycerine are 227 and 18·5 per cent.

PARCHMENT PAPER

(VEGETABLE PARCHMENT)

This is made by treating unsized paper with sulphuric acid. That used for the wrappers of cartridges of blasting explosives should be free from residual acid, which is not only injurious to the explosive, but will in time render the paper brittle. The acid converts part of the cellulose into a gelatinous form known as amyloid, which cements the fibres together and renders the paper impervious to liquids. It should be free from pinholes and specks. To test for permeability, a few drops of turpentine should be rubbed on the surface: it should not penetrate to the other side. To test for neutrality, some litmus solution is rubbed between two pieces of the paper: it should not change colour. It should be free from iron, lead, lime or any loading material. It should contain no mechanical wood pulp, as this on treatment with the sulphuric acid chars, leaving holes in the paper, through which nitro-glycerine can exude. C. N. Hake tests for mechanical pulp by immersing for four hours in milk of lime: there should be practically no yellowish-brown tint formed. He also immerses for five minutes in an aqueous solution of ferric chloride and potassium ferricyanide: there should be practically no blue tint.[2] In order to ascertain

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[1] *U.S. Bureau of Mines Bulletin*, No. 96, p. 54;

[2] *J. Soc. Chem. Ind.*, 1905, p. 915.

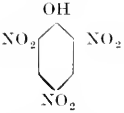
Parchment Paper

what fibres are present R. W. Sindall and W. Bacon disintegrate the paper by grinding it with water in a vertical coffee mill. They then examine it under the microscope. In staining with the iodine zinc chloride reagent the solution should be diluted, as the chemically modified fibres of vegetable parchment react so strongly with stain of the ordinary strength that all distinguishing tints are obscured.[1]

PICRIC ACID

(TRINITROPHENOL)

$C_6H_2(NO_2)_3OH$



Molecular weight 229·1

(*See also* Chapter XX)

Properties. Picric acid is soluble in about 15 parts of boiling water, but it requires 26 parts at 76° and 86 at 15°. The solution is intensely bitter, bright yellow in colour, and reddens litmus. In a stratum 1 inch in depth, the yellow colour of a solution of 1 part of picric acid in 30,000 of water is distinctly visible. The yellow colour of picric acid solutions is intensified by neutralization with an alkali. A cold saturated aqueous solution of picric acid gives a copious precipitate on adding hydrochloric acid.

Picric acid is readily soluble in alcohol, ether, chloroform, benzene, petroleum spirit, etc.; the last four solutions being colourless or nearly so. Such of the above solvents as are not miscible with water remove picric acid more or less perfectly from its aqueous solution, or that of a picrate which has been freely acidulated with sulphuric acid. Ether is preferable to chloroform for this purpose. A solution of picric acid in ether gives up the greater part of its colour to water, but on adding sulphuric acid or, still better, hydrochloric acid, the condition is reversed, the picric acid going chiefly into the ether.

All the above solutions of picric acid, including the aqueous, dye silk, wool, skin and other nitrogenous organic matters a yellow colour of a slightly greenish shade. The stain is not removable by water, but soap or alkali partly destroys it. Animal charcoal absorbs a large quantity of picric acid from its aqueous solution.

Detection. The yellow colour and extremely bitter taste of the aqueous solution of picric acid, the deepening of the yellow colour on adding excess of alkali, and the power possessed by the solution of the free acid of dyeing immersed wool or silk yellow are themselves important indications of its presence. In the presence of other colouring or interfering bodies, the picric acid may be

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[1] *Chem. Engineer*, 1915, 21, p. 75; *Analyst*, 1915, p. 248.

extracted from the aqueous solution by agitation with ether or amyl alcohol, after strongly acidulating with sulphuric acid. The picric acid may then be recovered by evaporating the ethereal solution or agitating it with a solution of sodium hydroxide, when it will pass into the alkaline liquid. The extraction of picric acid from an acidulated solution by ether, benzene, or amyl alcohol may be made quantitative.

A solution of picric acid is coloured an intense red by potassium cyanide or ammonium sulphide. The reaction with cyanide is very characteristic, but both these colorations are given by trinitro-cresol at once, whereas picric acid only gives them after some time or on heating. These two substances can be distinguished from one another from the fact that potassium picrate is only slightly soluble in cold water, whereas the trinitro-cresylate is readily soluble. If caustic potash be added to a cold saturated solution of picric acid the picrate separates in yellow needles. The pyridine salts behave in the reverse manner.[1]

An aqueous solution of picric acid is not precipitated on adding neutral lead acetate, but basic or ammoniacal lead acetate gives a bright yellow precipitate even with very dilute solutions of picric acid.[2]

Picric acid is not precipitated from its aqueous solution by copper sulphate; but the ammonio-sulphate produces a bright green precipitate, which is insoluble in ammonia and is decomposed by washing with water. A solution containing 1/10,000 of picric acid gives a distinct precipitate with ammonia-copper sulphate in twenty-four hours.

If a solution of picric acid be treated with zinc and dilute sulphuric acid, a turbid yellowish-red solution is obtained, which, when poured off from the excess of zinc and mixed with alcohol, develops a green colour, changing through blue to a violet.

Picric acid forms highly insoluble compounds with many of the vegetable alkaloids, and the insolubility of the cinchonine salt has been employed for the determination of picric acid. According to Kast picric acid and trinitro-cresol can be detected when diluted with the following quantities of water by means of cinchonine and acridine:

	Cinchonine	Acridine
Picric acid	5,000	50,000
Trinitro-cresol	17,000	100,000

Of the compounds of picric acid with solid hydrocarbons, that with naphthalene, $C_{10}H_8 + C_6H_3(NO_2)_3O$, is almost the only one precipitated when

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[1] H. Kast, *Spreng- und Zündstoffe*, p. 974.

[2] If the precipitate is decomposed by dilute sulphuric acid and the filtered solution rendered ammoniacal and evaporated to dryness, a residue is obtained which gives a deep brown colour on heating with potassium cyanide. This behaviour distinguishes picric acid from quercitron and such other vegetable yellow colouring-matters as are precipitated by basic lead acetate.

Picric Acid

the cold alcoholic solution of the hydrocarbon is mixed with a cold alcoholic solution of picric acid. It forms stellate groups of golden-yellow needles, melting at 149°. The formation of naphthalene picrate may be employed to distinguish picric acid from similar nitro-compounds.

Estimation.

A solution of cinchonine sulphate acidulated with sulphuric acid is added to the picric acid solution. The precipitate of cinchonine picrate, $C_{20}H_{24}N_2O(C_6H_3N_3O_7)_2$, is washed with cold water, rinsed off the filter into a porcelain crucible or dish, the water evaporated on the water-bath, and the residual salt weighed. The yellow, intensely bitter alkaloid berberine, is said to precipitate picric acid so perfectly that, on mixing the picric and alkaloidal solutions in equivalent proportions and filtering, the filtrate is colourless and perfectly free from bitter taste.

Acridine has been suggested by Anschütz [1] as a suitable reagent for the determination of picric acid, the hydrochloride being used as a precipitant for metallic picrates and a solution of the free base in benzene for the picric acid compounds of hydrocarbons. Busch and Blume state, however, that the results are inaccurate if the solution be hot, as acridine picrate is decomposed by warm water. They recommend precipitation with nitron, which forms a picrate very insoluble in water and even in 50 per cent. alcohol. The solution is precipitated with nitron acetate in a boiling dilute solution acidified with sulphuric acid. The precipitate is filtered off and dried at 110° and weighed. Its weight multiplied by $\frac{229}{541}$ gives the quantity of picric acid. The solution must be free from chlorides, bromides, iodides, perchlorates, nitrates, and chromates.[2]

Picric acid may be titrated with standard alkali and phenolphthalein, but according to Minovici and Kollo excess of alkali is required with lacmoid or phenolphthalein, whereas with methyl red (p. methyl-amino-azo-benzene-o-carboxylic acid) as indicator the colour change is sharp and correct.[3] The process is applicable to the ethereal or benzene solution if diluted with alcohol.

Examination.

The nitrogen may be determined in picric acid by the Kjeldahl method, or by titration with chloride or by the decomposition flask method.

General impurities and adulterations may be detected and determined by treating 2 g. of the finely powdered sample with 50 c.c. of methylated ether or benzene. The picric acid dissolves, while any picrates, nitrates, oxalic acid, boric acid, sodium sulphate, alum, sugar, etc., will be left insoluble, and, after removal of the liquid, may be readily identified and determined. For the detection and determination of *water* and *oxalic acid*, 50 c.c. of warm benzene

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[1] B., vol. 17, p. 438 ; *J. Soc. Chem. Ind.*, 1884, vol. 3, p. 324.

[2] M. Busch and G. Blume, *Ang.*, 1908, p. 354.

[3] S. Minovici and C. Kollo, *Bull. Acad. Sci. Roumanie*, 1914–15, 3, p. 61 ; *Abst. Chem. Soc.*, 1915, ii, p. 383.

may be advantageously substituted for the ether. Sugar and boric acid may be separated from the other impurities by treating the residue insoluble in ether or benzene with rectified spirit. If *boric acid* is present the alcoholic solution will burn with a green flame. *Sugar* may also be sought for by neutralizing the aqueous solution of the sample by sodium carbonate, evaporating to dryness, and extracting with proof-spirit, which will dissolve any sugar and leave the sodium picrate insoluble.

Sulphuric, hydrochloric, and oxalic acids, and their salts, may be detected by adding solutions of barium, silver, and calcium, respectively, to the warm, filtered, aqueous solution of the sample. *Free sulphuric acid* might be detected by dissolving the sample in warm benzene, agitating the solution with warm water, removing the benzene layer, and again agitating the aqueous liquid with benzene, till all yellow colour is removed. On then titrating the aqueous liquid with standard alkali, the volume required for neutralization will correspond to the free sulphuric or other mineral acid of the sample.

It is possible that commercial picric acid occasionally contains a *nitrophenolsulphonic acid.* Such an impurity would be indicated by the presence of sulphates in the residue obtained on igniting with a large excess of alkali.[1]

A determination of the melting-point indicates whether the sample contains organic impurities. That of the pure substance is 122°, but the commercial material usually melts a degree or two lower. When examining for these impurities it is best to remove the picric acid by precipitation with naphthalene in alcoholic solution, and then investigate the substances remaining in solution. 2 : 4-dinitro-phenol is a frequent impurity ; its melting-point is about 114°.

Trinitro-toluene may be detected by the intense red coloration it gives when boiled with a dilute solution of caustic alkali. Trinitro-benzene gives a similar colour at once without heating. Trinitro-cresol also gives a red coloration with potash, and Kast makes use of it to determine the amount of this substance colorimetrically. About 0·1 gramme of the picric acid is weighed out and dissolved in 50 c.c. of a 1 per cent. solution of caustic potash. It is heated to 80°, cooled and allowed to stand for some time for potassium picrate to separate. The clear liquid is then poured off and its colour is compared with that of a solution containing known quantities of trinitro-cresylate, diluting if necessary with a solution of pure picrate. A content of 0·05 to 0·3 per cent. trinitro-cresol gives the most satisfactory results. The solutions should be compared at a temperature of 18° to 20°.[2]

A method of estimating small proportions of dinitro-phenol in picric acid is by treating the aqueous solution of the sample with bromine, as proposed by A. H. Allen.[3] With dinitro-phenol the following reaction occurs :

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[1] *See Analyst,* vol. 13, p. 43.

[2] *Spreng- und Zündstoffe,* p. 974.

[3] *Jour. Soc. Dyers, etc.,* vol. 4, p. 84.

$C_6H_3(NO_2)_2OH + Br_2 = HBr + C_6H_2Br(NO_2)_2OH$. With picric acid, bromine reacts as follows:

$$C_6H_2(NO_2)_3OH + Br_2 + H_2O = HBr + HNO_3 + C_6H_2Br(NO_2)_2OH.$$

In each case 2 atoms of bromine enter into the reaction, with formation of a bromo-dinitro phenol (the same in each case), and 1 molecule of hydrobromic acid. But in the case of picric acid nitric acid is formed in addition, and hence the acidity of the liquid at the end of the reaction would be greater the larger the proportion of picric acid present. If the bromo-dinitro-phenol and excess of bromine [1] were removed by agitation with ether or similar solvent, the acidity of the aqueous liquid could be ascertained with great accuracy by titration with standard alkali.

The reaction between bromine and dinitro-phenol occurs promptly, but in the case of picric acid it is gradual. In twelve hours it is complete, but the change that occurs in the course of a few minutes is negligible. This fact enables the reaction with bromine to be utilized for the direct estimation of the dinitro-phenol, instead of for its indirect estimation (by estimating the picric acid), as when the acidity is ascertained. The following method of operating was found by the author to be the most satisfactory: 1 g. of the sample of picric acid is dissolved in about 100 c.c. of warm water. A saturated solution of bromine in water is diluted with twice its measure of water in a large tapped and stoppered separator, and from this run into a burette. From this burette a definite volume of the bromine solution, which is approximately of 1 per cent. strength, is run into a flask and an equal measure into another similar flask, both of which are immediately closed. The picric acid solution is then poured into one of the flasks, the last drops rinsed in without delay, and then an excess of a solution of potassium iodide at once added to the contents of both flasks. The liberated iodine is then determined by titration with a decinormal solution of sodium thiosulphate (hyposulphite) in the usual way.[2] From the difference in the volume of the solution required in the two experiments the amount of bromine which has reacted with the dinitro-phenol is easily found. *Dinitro-phenol* reacts with 86·84 per cent. of bromine, taking up 43·42 per cent. *Mononitro-phenol*, if present, which is improbable, would react with 229·8 per cent. of bromine, taking up 114·9 per cent. to form the compound $C_6H_2Br_2(NO_2).OH$. Allen verified these reactions by experiments on specially prepared mono- and dinitro-phenol. When the process is applied to commercial picric acid the results are liable to be somewhat in excess of the truth, owing to slight action of the bromine on the picric acid itself.

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[1] If preferred, before extracting with ether the excess of bromine may be got rid of by adding potassium iodide and then sufficient sodium thiosulphate to react with the iodine liberated.

[2] Allen found iodine to be wholly without action on solutions of either mono-, di- or tri-nitro-phenol.

Density of picric acid.

Picric acid which has been melted has a density of 1·68 to 1·70. On solidifying there is an apparent expansion, which, however, is partly or wholly due to the manner in which it crystallizes: needle-like crystals are formed between which small interstices are left. By compression somewhat higher densities can be attained; Dautriche obtained the following:

Pressure		Mean density
kg./cm.²	tons/in.²	
275	1·75	1·315
685	4·35	1·480
1375	8·73	1·614
2060	13·1	1·672
2750	17·5	1·714
3435	21·8	1·731
4125	26·2	1·740

whence it is concluded that the limiting density for the compressed material is about 1·76.[1]

PICRATES AND TRINITRO-CRESYLATES

The composition and temperatures of ignition of a large number of metallic picrates were investigated by Silberrad and Phillips.[2] and the formation and explosibility of various picrates and trinitro-cresylates by Kast.[3] The picrates of lead, calcium, barium, potassium, and copper explode when heated, the lead compound being much more violent than the others. The picrates of sodium, zinc, silver, magnesium and iron explode with considerably less violence: those of ammonium, mercury and aluminium, like picric acid itself, do not explode when heated in the ordinary way.

The trinitro-cresylates behave very similarly to the corresponding picrates. The lead salts are also by far the most sensitive to blows, being about as dangerous in this respect as nitro-glycerine, blasting gelatine and dry-guncotton. The salts of the other heavy metals, such as copper, silver, iron, calcium, and barium are also somewhat sensitive: more so than picric acid. The salts of sodium, potassium and ammonium are less sensitive, and those containing water of crystallization are less so than the dried substances.

The action of solutions of picric acid and trinitro-cresol upon different metals was investigated by Kast. Plates of metal 5 × 10 cm. were placed

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[1] *P. et S.*, vol. 16, 1912, p. 28.

[2] *Trans. Chem. Soc.*, 1908, p. 474.

[3] *S.S.*, 1911, pp. 7, 31 and 67.

Picrates

in mixtures of 50 g. picric acid or trinitro-cresol and 200 g. water for four weeks. It was then found that the following quantities of the metals had been dissolved :

	Picric acid	Trinitro-cresol
Lead	3·91 g.	4·15 g.
Iron	13·71 g.	3·78 g.
Zinc	18·86 g.	0·48 g.
Copper	2·37 g.	1·04 g.
Brass	1·19 g.	1·02 g.
Aluminium	small quantity	small quantity

Saposhnikof tried the effect of molten picric acid on metals under conditions more nearly resembling those that prevail in a shell that is filled with the melted explosive. One g. of the finely divided metal was placed in a beaker with 2 g. of picric acid and kept at a temperature of 125° for eight and a half to nine hours. The weights of metal that had been dissolved were :

Lead	0·2798 g.
Iron	0·1530 g.
Zinc	0·2046 g.
Copper	0·1754 g.
Aulminium	0·0488 g.
Nickel	0·1862 g.
Tin	0

Ammonium picrate, $C_6H_2(NO_2)_3ONH_4$, mixed with potassium nitrate in the proportion 43 : 57 is used in the exploders of lyddite shell. Numerous proposals have been made in patent specifications and elsewhere to use other picrates in explosive mixtures, but these have never come into general use.

SULPHUR

S. Atomic weight 32·06

(*See* Chapter V)

Impurities. This should be finely ground roll sulphur free from acid, arsenic and ash. To test for acid, boil with water and test with litmus-paper ; there should not be more than a very faint reddening. Arsenic gives the sulphur an orange-yellow colour ; to test for it, 5 g. are treated for a quarter of an hour with 100 c.c. ammonia at 50° to 60°, and the liquid is filtered and acidified with hydrochloric acid : there should be no weighable precipitate even after adding sulphuretted hydrogen water. The residue on ignition should not exceed 0·15 per cent.

Estimation. To determine the sulphur in gunpowder, it is evaporated not less than three times with strong *aqua regia*. The residue is moistened with hydrochloric acid and again evaporated to drive off the nitric acid, then dissolved in water, filtered and precipitated with barium chloride solution, using only slightly more than is actually required. It is not essential to destroy entirely all the carbon in the powder.

Roll sulphur is readily soluble in carbon bisulphide, but flowers of sulphur leave a residue of 20 to 30 per cent. insoluble in this solvent. Sulphur is moderately soluble in acetone, ether, alcohol, and other organic solvents. It may be separated from nitro glycerine by dissolving the latter in acetic acid of 70 per cent. strength: sulphur is practically insoluble in this solvent.[1] Sulphur oxidizes slowly at 100°, especially if nitrates be present: for the determination of moisture in black powder, etc., the material should not be heated above about 70°.

TETRANITRO-METHANE

$C(NO_2)_4$. Molecular weight 196

This substance is formed when various substances are treated with strong nitric acid, but is best prepared by the action of strong nitric acid on acetic anhydride in the cold.

$$4(CH_3.CO)_2O + 4HNO_3 = C(NO_2)_3 + CO_2 + 7CH_3.COOH$$

The yield is nearly theoretical if the reaction is allowed to proceed at the ordinary temperature for eight days.[2] It is said to be formed sometimes during the manufacture of trotyl.

It is a heavy, faintly yellow liquid boiling at 126°, with only slight decomposition. Its density is 1·65 at 13°. It solidifies at about 13°. It is more stable than the lower nitrated derivatives of methane, but decomposes in contact with copper, forming compounds which are explosive.[3] With sodium ethylate it reacts explosively with great violence.[4] It is too volatile to use as a constituent of explosives.

WOOD-MEAL

(WOOD PULP, WOOD FLOUR)

This is used not only in the manufacture of nitro-glycerine explosives, but also of linoleum, and as an inert absorbent in other industries. The species of wood employed are limited by considerations of colour and weight to the white non-resinous conifers and broad-leafed woods: spruce, white pine and poplar are those most often used. The wood, stripped of bark, is reduced to chips,

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[1] *U.S. Bureau of Mines Bulletin*, No. 51, p. 42.

[2] *See* F. D. Chattaway, *Trans. Chem. Soc.*, 1910, p. 2099.

[3] W. R. E. Hodgkinson and F. R. J. Hoare, *J. Soc. Chem. Ind.*, 1914, p. 522.

[4] A. K. Macbeth, *Ber.*, 1913, p. 2537.

Wood-Meal

and then ground in stone mills or in steel burr roller mills, the former being used almost exclusively in Europe, especially in Scandinavia where water-power turbines are employed. The mills are enclosed, and sufficient water or steam is passed in to prevent firing. The fine material is drawn or blown through iron pipes to a screen of bronze wire or bolting cloth. It is then sacked or compressed into bales. Before the war Norwegian wood flour was delivered in the U.S. Atlantic ports for $12·50 to $15 (£2 12*s.* to £3 2*s.* 6*d.*) per ton, and sold there in competition with the local product. The absorptive powers may be improved by boiling with water and drying. In 1900 nearly ten million pounds of wood-meal were used in the manufacture of dynamite in the United States, and in 1909 probably about twenty million pounds.[1]

Wood-meal for the manufacture of explosives should be free from acid and foreign substances, especially particles of metal and grit. The moisture should not exceed 8 or 10 per cent., nor the ash 0·5 per cent. It should absorb nitro-glycerine readily. It should not contain chlorides or hypochlorites or other bleaching material which would attack the nitro-glycerine and affect the heat test. The heat test of the material mixed with blasting gelatine should be taken. Different factories use meal of different degrees of fineness: it is sometimes required that the whole shall pass through a sieve of 50 meshes to the inch and not more than 30 per cent. through a 100-mesh sieve. It should not contain much resin or tannin. The resin may be extracted by ether. Extraction with alcohol will remove also the tannin and some other constituents. Water and dilute acids also remove part of the material. It was found by Snelling and Storm that successive extractions removed the following amounts, calculated on the dry weight, from four samples of wood pulp:[2]

Extraction with	1	2	3	4	Mean
Ether	2·66	2·78	2·09	1·95	2·37
Cold water	2·57	2·89	2·23	2·84	2·63
Cold hydrochloric acid (1 : 10) . .	1·41	0·42	0·53	1·03	0·85
Boiling hydrochloric acid (1 : 100) . .	5·91	1·75	3·93	4·83	4·11
Insoluble residue	87·45	92·16	91·22	89·35	90·04

Therefore if wood-meal is determined by weighing the residue, this should be divided by 0·9 to give approximately the dry weight. If the weight in the air-dry condition be required, a further 10 per cent. should be added on.

Wood-meal is detected by its appearance under the microscope, and by the coloration it gives with phloroglucinol reagent, which is made by dissolving

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[1] F. W. Kressmann, *Met. and Chem. Eng.*, 1916, p. 372.

[2] *U.S. Bureau of Mines Bulletin*, No. 51, p. 48.

Wood-Meal

1 gramme of phloroglucinol in 15 c.c. of alcohol and 10 c.c. of syrupy phosphoric acid. If a little of the meal be rubbed with 0·5 c.c. of this, it acquires a rose colour changing to carmine. Under the microscope the proportion of grains thus coloured can be roughly estimated.[1]

For the determination of ligno-cellulose in wood-meal, *see* J. F. Briggs, *Analyst*, 1916, p. 113.

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[1] *Allen's Commercial Organic Analysis*, vol. i., 1909, p. 462.

Wood-Meal

APPENDICES

APPENDIX I

REGULATIONS OF THE IMPERIAL GERMAN RAILWAY COMMISSION

Dangerous goods are divided into the following classes:

I. Explosible goods.
II. Spontaneously combustible goods.
III. Combustible liquids.
IV. Poisons.
V. Corrosive goods.
VI. Goods liable to putrefaction.

Class I is subdivided into:

I*a*. Explosives.
I*b*. Ammunition.
I*c*. Matches and fireworks.
I*d*. Compressed and liquefied gases.
I*e*. Goods which in contact with water give gases that are combustible or support combustion.

Class I*a* is further subdivided into:

A. Blasting explosives.
B. Propellents.
C. Other explosives.

These again are split up into groups according as they satisfy the tests laid down. Different tests are specified for each sub-group, and the results are compared with those given by certain standard substances.

A, group 1 may be sent in unlimited quantities as ordinary goods.
2 quantities of 200 kg. only as ordinary goods.
3 truck loads only.
B, group 1 may be sent in unlimited quantities as ordinary goods.
2 truck loads only.

The sub-groups with their respective standards are as follows:

Sub-group	Description	Standard
A. 1 (*a*)	Ammonium nitrate explosives	Donarite
1 (*b*)	Organic nitro-compounds	Picric acid
1 (*c*)	Nitro-cellulose with 25 per cent. water or alcohol or compressed with 15 per cent. water.	
1 (*d*)	Nitrate mixtures	Sprengsalpeter
2 (*a*)	Organic nitro-compounds insoluble in water with 25 per cent. water.	Tetranitro-methylaniline.
2 (*b*)	Chlorate and perchlorate explosives.	Cheddite.
2 (*c*)	Nitrated chlorhydrins.	
2 (*d*)	Triplastite.	
2 (*a*)	Organic nitro-compounds not in sub-groups 1 (*b*) or 2 (*a*).	Tetranitro-methylaniline.
3 (*b*)	Nitro-cellulose unpressed with 15 per cent. water, or compressed dry in cartridges, paraffined.	
3 (*c*)	Chlorate and perchlorate explosives not in 2 (*b*).	Silesia I.
3 (*d*)	Black powder, and similar explosives not in 1 (*d*).	Black powder.
3 (*e*)	Dynamite, etc.	Blasting gelatine or Guhr dynamite.
3 (*f*)	Ammonium nitrate explosives not in 1 (*a*).	Gelatine dynamite.
3 (*g*)	Samples.	Blasting gelatine or Guhr dynamite.
B. 1	Gelatinized smokeless powders satisfying sundry tests.	
B. 2	Gelatinized smokeless powders not satisfying the tests. Ungelatinized smokeless powders. Black powder pressed and granulated, etc. Thoroughly gelatinized cords of powder and articles made from them.	

TESTS

Applied to Explosives by the German Railway Commission

A. Blasting Explosives

I. *Ammonium Nitrate Explosives*

As the standard of comparison *Donarite* is used having the following composition:

Ammonium nitrate	80 per cent.
Trinitro-toluene.	12 ,,
Rye flour	4 ,,
Nitro-glycerine	4 ,,

The solid constituents are dried, passed through a sieve with 256 meshes to the sq. cm. (40 meshes to the inch), and mixed together, and then with the nitroglycerine, until the mixture is quite uniform.

The tests consist of:

1. Chemical analysis.
2. Behaviour to litmus paper.
3. Exposure to high temperature.
4. Shaking test.
5. Behaviour on ignition.
6. Sensitiveness to mechanical influence (blows, friction).
7. Addition of water (separation of nitro-glycerine).

Preparation of the explosive. Care must be taken that the sample correctly represents the bulk of the explosive. The sample is to be dried over calcium chloride. It can be reduced to the required state of division in a mortar.

1. *Chemical analysis.* The proportions must be accurately determined, especially of such substances as increase the explosibility of the explosive (*e.g.* nitro-glycerine).

2. *Behaviour to litmus paper.* 1 g. of the explosive is rubbed up with 3 c.c. of distilled water and the mixture is tested with sensitive blue litmus paper. Comparative tests are carried out before and after hot storage (*see* 3). There must be no increase of any acid reaction after the storage. Donarite has a slight acid reaction before and after hot storage.

3. *Storage of the explosive at 75° C.* Two samples of 10 g. each of the undried explosive are to be placed in lightly closed weighing bottles, 35 mm. in diameter and 50 mm. high. The bottles are to be kept for forty-eight hours in a drying oven heated at 75° C. It should then be ascertained whether there is any alteration in the weight of the samples or their condition (appearance, reaction, smell). Donarite only suffers slight loss of weight, and there are no serious signs of decomposition.

4. *Shaking test for separation of ingredients.* 10.0 g. of the explosive are placed in a dry wide-mouthed bottle of 150 c.c. capacity and shaken backwards and forwards horizontally in a shaking machine 150 times a minute for five hours. It is then ascertained whether the ingredients have separated from one another, if necessary by tests 5 and 6 below. Donarite shows no change.

5. *Behaviour on ignition.* (*a*) Ignition with safety fuse: 3 g. of the powdered explosive are placed in an ordinary test-tube, and a level surface is produced by gentle tapping. On the middle of this surface a piece of slow burning safety fuse (1 metre in 100 secs.) is gently placed and ignited. This experiment is carried out twice with each explosive. Donarite is not ignited.

(*b*) Throwing portions of the powdered explosive into a red-hot iron basin: A hemi-spherical basin 1 mm. thick and 12 cm. diameter is heated to a red heat on the ring of a retort stand by means of a triple burner. At first only small portions are thrown in (0·5 g.). If no detonation takes place, the quantity thrown in at one time is gradually increased up to 5 g. The experiment is repeated twice. Donarite does not explode.

Note. The manner in which the explosive burns is observed, and the time that elapses from throwing into the basin to the extinction of the flame.

This test must be carried out with proper precautions. It is recommended that the work be carried out in a good draught and behind two thick sheets of glass. Safety spectacles should be worn.

(*c*) Heating small portions to the ignition point in test-tubes placed in a bath of Wood's metal: An iron basin 14 cm. diameter and 7 cm. high is filled to within 2 cm. of the top with Wood's metal. In the centre of the bath a thermometer (0°–360° C.) is immersed 30 mm. deep; it is divided into whole degrees and protected against the effects of explosions. Around the thermometer at a distance of 50 mm. are placed three test-tubes, each 15 mm. internal diameter and 120 mm. long, and immersed 20 mm. deep in the bath. Each test-tube contains 0·2–0·5 g. of the sample, and is placed in the bath at 100°. The temperature of the metal bath is then raised 20° a minute, until ignition occurs or the temperature reaches 320°. Donarite does not ignite below 250°.

NOTE. This test should be carried out behind a protecting screen.

(*d*) Burning large quantities in iron boxes in a wood fire: The box is made of sheet iron, 1 mm. thick: it is cubical in shape, edge 85 mm.; it is riveted and the top edge is turned over 8–9 mm. It has a movable lid and is filled with the explosive (0·5 to 1 kg.). The lid is placed on and fastened with iron wire bound crosswise round the box, which is then placed in a brisk wood fire and kept there at least ten minutes. The experiment is to be repeated once. Donarite does not explode.

NOTE. This test must be carried out either in the open not less than 100 metres from inhabited buildings, or else in a place that is well protected from the effects of an explosion. The box to be placed on the fire with care, preferably by means of a mechanism that can be worked from the place of observation. With substances that are not very explosive the box can be laid on by hand, if the place of observation is near: but in this case it should be wrapped up well beforehand in brown paper, so that the explosive may not be ignited too soon through gaps in the iron box.

6. *Mechanical sensitiveness.* (*a*) Blows under the falling weight.

Preparation of the sample. It must be finely divided, and dried twenty-four hours in a vacuum desiccator with calcium chloride, the layer of explosive being not more than 1 cm. thick.

The apparatus consists of a falling weight with an arrangement for suspending it, two rods to guide it, and an anvil of hardened steel let into a support of cast iron in a masonry foundation. About 0·05–0·1 g. of the explosive is spread in a thin layer on the anvil and covered with a short bolt of hardened steel. Instead of laying the explosive loose on the anvil, use may be made of a mould. Every explosive must be tested with a 2 kg. and a 10 kg. weight. At each height of fall six tests are to be carried out, each time with a fresh quantity; in each test the weight is only to be allowed to fall once. The temperature must be 15–20° C. That height at which the explosive begins to detonate regularly (once in six tests) with a distinct report or total ignition is the measure of the sensitiveness. The anvil and bolt are to be cleaned carefully before each test.

(*b*) Friction in an unglazed porcelain mortar.

Preparation of sample, as in 6 (*a*).

The mortar is of unglazed porcelain, 10 cm. internal diameter and 6 cm. high, with an unglazed pestle: the mortar is to be cleaned carefully before the test.

The friction test is to be carried out with 0·05 g. of the substance at the ordinary temperature. The test is to be repeated twice. With Donarite a slight crackling is heard and a little local blackening takes place.

7. *Addition of water.* Take a cylindrical glass tube about 20 cm. long and 25 mm. wide drawn out at one end; where it is drawn out place a wad of glass wool and fix the tube vertically. Press 50 g. of the explosive firmly in and pour 100 c.c. of distilled water on to it. The column of water is maintained at its original height by occasional additions, until 50 c.c. have flowed through. No nitro-glycerine must separate from the solution that has come through.

A. II. *Organic Nitro-Compounds and Mixtures containing them.*[1]

As the standard of comparison for nitro-compounds, etc., of Group 1, finely powdered *picric acid* is used with a melting-point not below 120° C.; for Groups 2 and 3 finely powdered *tetranitro-methyl-aniline* with a melting-point not below 124° C.

The tests consist of:

1. Chemical analysis and establishment of identity (melting-point, etc.).
2. Solubility in water, and tendency to form salts (behaviour towards litmus paper).
3. Exposure to high temperature.
4. Behaviour on ignition.
5. Sensitiveness to mechanical influence (blows, friction).

Preparation of the nitro-compound. Before examination, the substance is to be ground up fine and sifted or otherwise comminuted, and then dried for twenty-four hours in a vacuum desiccator over calcium chloride.

1. *Melting-point determination.* A small portion is placed in a fine tube and melted, using an accurate thermometer.

NOTE. This test must be carried out with proper precautions.

2. (*a*) *Solubility in water.* 1 g. of the substance is placed in a stoppered bottle with 100 c.c. of distilled water at 15°–20° C. and shaken repeatedly for half an hour, the undissolved material is then collected on a weighed filter, dried and weighed.

(*b*) *Behaviour to litmus paper.* The solution obtained by (*a*) is tested with sensitive blue litmus paper. In order to detect any red coloration the paper must be washed with water.

(*c*) *Tendency to form dangerous salts.* (i) The solution obtained by (*a*) is left for twenty-four hours in contact with a clean piece of lead sheet free from grease. The solution is removed by washing with water and, if necessary, wiping with a damp pad of cotton-wool, and then it is ascertained whether there has been any action, such as formation of salt.

(ii) 0·5 g. is shaken for five minutes with a solution of 1 g. of sodium hydroxide in 10 c.c. water. To the filtrate an excess of hydrochloric acid is added. A precipitate indicates a tendency to form salts.

(iii) The solution obtained in (2) is slightly acidified with acetic acid and then a little acetate of lead is added. If a precipitate is formed, it is dried and tested for sensitiveness according to paragraph 6 under ammonium nitrate explosives.

3. *Storage of the nitro-compound at 75° C.* As described in paragraph 3 of the

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[1] The word nitro-compound is here used in its scientific sense and does not include nitro-cellulose and nitro-glycerine as in the English regulations.

directions for testing ammonium nitrate explosives. If there be a decided alteration in the appearance or weight of the substance, it should be tested by the methods of paragraph I 6 to see if there has also been an alteration in its sensitiveness. The standard substances show no alteration.

4. *Behaviour on ignition.* (*a*) Ignition with safety fuse. As in 5 (*a*) of the instructions for testing ammonium nitrate explosives. Picric acid is not ignited.

(*b*) Throwing portions into a red-hot iron basin. As in 5 (*b*) of the instructions for testing ammonium nitrate explosives. Picric acid and tetranitro-methyl-aniline do not explode.

(*c*) Heating small portions to the ignition point in test-tubes in a bath of Wood's metal. As in 5 (*c*) of the instructions for testing ammonium nitrate explosives. Picric acid ignites at about 300°, but does not explode. Tetranitro-methyl-aniline ignites at about 190° and puffs off without exploding.

(*d*) Burning a large portion in an iron box in a wood fire. As in 5 (*d*) of the instructions for testing ammonium nitrate explosives. Picric acid burns rapidly but does not explode. Tetranitro-methyl-aniline burns with occasional puffs.

5. *Mechanical sensitiveness.* As in 6 of the instructions for testing ammonium nitrate explosives. When rubbed in the porcelain mortar the standard explosives become brown but do not crackle.

A. III. *Nitrated Chlorhydrins*

There is a danger that nitrated chlorhydrins made from chlorhydrin containing glycerine may contain nitro-glycerine. Any considerable admixture of this kind can be detected by comparing with pure dinitro-chlorhydrin in the falling weight and friction tests (*see* I. 6 (*c*) and (*b*)).

A. IV. *Nitro-cellulose* (*Gun-cotton, Collodion Cotton*)

The tests consist of:

1. Establishment of identity.
   - (*a*) Determination of nitrogen.
   - (*b*) Temperature of ignition.
2. Determination of the amount of water or alcohol.
3. Estimation of any additions (potassium or barium nitrate, paraffin).
4. Determination of the stability at 145° C.

1. (*a*) *Nitrogen determination.* This may be carried out by the Schultze-Tiemann (Schlösing) or Lunge method.

1. (*b*) *Temperature of ignition.* About 0·1 g. of the dried nitro-cotton is put into a test-tube 125 mm. long, 15 mm. internal diameter, and 0·5 mm. thick in the wall. This is placed in an oil-bath previously heated to 100° so that exactly 45 mm. of the tube are in the oil and 40 mm. project above the lid of the oil-bath. The middle of the bulb of the thermometer used must be at the same level as the bottom of the test-tube. The temperature of the oil is raised about 5° C. per minute, so that 180° is reached in sixteen minutes.

2. *Percentage of water or alcohol.* 10 gr. of the moist nitro-cellulose are dried

in a glass basin 30 mm. high and 55 mm. in diameter, provided with a ground-on lid, at 60° C. until the weight is constant. The test is repeated twice.

3. (*a*) *Estimation of additions soluble in water* (potassium, barium nitrate). 10 g. of the dried nitro-cellulose in a weighed filter are washed out with hot distilled water until nothing more goes into solution. The filter with the residue is dried at 60° until the weight is constant.

(*b*) *Paraffin* is determined by extraction with ether.

4. *Stability test at* 145° *C*. Quantities of 0·1 g. dry nitro-cellulose (containing not more than 0·5 per cent. moisture) are placed each in a little glass flask 10 mm. wide and of about 1 c.c. capacity. The flasks are closed by means of tinfoil and heated to 145° in the apparatus to be described. Purified nitro-cellulose must withstand the heating for five minutes without igniting.

The test is carried out as follows: A cylindrical copper bath 10 cm. diameter is filled with machine oil (*see* Fig. 158). The lid has five holes: one is for the thermometer, the other four to take copper tubes, which are inserted with cork stoppers. The tubes must have an internal diameter of 13 mm. and be immersed 4 cm. in the oil. The bottoms of the tubes must be covered with a thin layer of asbestos. When the bath has been heated to 145°, the flasks containing the nitro-cellulose are put into the copper tubes. It is then ascertained whether the four portions ignite in five minutes.

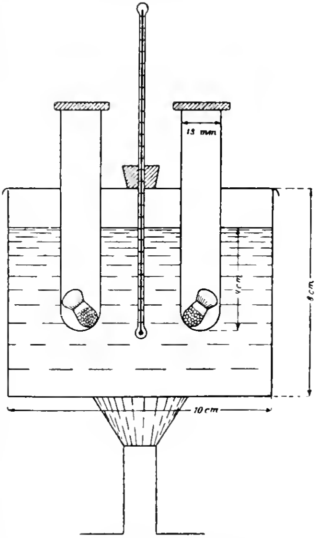

FIG. 158. Stability Test at 145°

A. V. *Chlorate and Perchlorate Explosives*

As standard of comparison for these explosives in Group 2, *Cheddite* is used, of the composition:

Potassium chlorate	79·0 per cent.
Nitro-naphthalene	1·0 ,,
Dinitro-toluene	15·0 ,,
Castor-oil	5·0 ,,

(The nitro-naphthalene, dinitro-toluene, and castor-oil are melted up together in a water bath, and then the dry finely powdered chemically pure potassium chlorate is uniformly kneaded into the molten mass. Samples are taken and analysed to ascertain that the mixture is uniform.)

As standard of comparison for Group 3, *Silesia I* is used, of the composition:

Potassium chlorate	85·0 per cent.
Colophony	15·0 ,,

(Made by intimately mixing the powdered, sifted, dry constituents.)
The tests consist of:

1. Chemical analysis, especially to ascertain the uniformity of the composition.
2. Behaviour to litmus paper.
3. Exposure to high temperature.
4. Exposure to moist and dry air.
5. Shaking test.
6. Behaviour on ignition.
7. Mechanical sensitiveness.

2. *Behaviour to litmus paper.* As in I 2. Cheddite and Silesia I give no acid reaction

3. *Storage at 75° C.* Cheddite and Silesia I do not alter appreciably.

4. *Exposure alternately to moist and dry air.* Two portions of 10·0 g. each are kept alternately for forty-eight hours in moist air (under a bell-jar over water) and then forty-eight hours in dry air (in a desiccator). This is done three times. The mechanical sensitiveness is then tested, also the behaviour on ignition, by the methods in I 5 and 6. Cheddite and Silesia I do not alter.

5. *Shaking test.* As in I 4. Cheddite and Silesia I do not alter.

6. *Behaviour on ignition.* (*a*) With safety fuse. As in I 5 (*a*). Cheddite and Silesia I do not ignite.

(*b*) Throwing into red-hot iron basin. As in I 5 (*b*). Cheddite and Silesia I burn rapidly, but do not explode.

(*c*) Determination of ignition point in metal bath. As in I 5 (*c*) Cheddite and Silesia I do not ignite below 200°.

(*d*) Burning in wood fire. As in I 5 (*d*). Cheddite burns rapidly with slight deflagration, Silesia deflagrates vigorously.

7. *Mechanical sensitiveness.* (*a*) Falling weight. As in I 6 (*a*).

(*b*) *Friction* in mortar. As in I 6 (*b*). Cheddite and Silesia I crackle considerably, but the explosions are only local.

A. VI. *Black Powder and similar Explosives*

As standard of comparison for Group 1 (*d*) *Sprengsalpeter* is used, of the composition:

Sodium nitrate	75 per cent.
Sulphur	10 ,,
Brown charcoal	15 ,,

For Group 3 (*d*) a *Sporting Powder* ground to dust and having the composition:

Potassium nitrate	75 per cent.
Sulphur	10 ,,
Alder charcoal	15 ,,

The tests consist of:

1. Chemical analysis.
2. Behaviour to litmus paper.
3. Exposure to high temperature.
4. Behaviour on ignition.
5. Mechanical sensitiveness.

1. *Chemical analysis.* Special care should be taken to ascertain what additional substances are present besides those in the standard explosive.

2. *Behaviour to litmus paper.* As in I 2. The explosives must not be more than slightly acid.

3. *Warm storage.* As in I 3. The standard powder only loses slightly in weight.

4. *Behaviour on ignition.* (*a*) With safety fuse. As in I 5 (*a*). The standard powder burns but does not detonate.

(*b*) In red-hot iron basin. As in I 5 (*b*). Sprengsalpeter ignites after a few seconds and burns away rapidly, but does not detonate; the sporting powder ignites at once but does not explode.

(*c*) In metal bath. As in I 5 (*c*). The standard powder ignites at about 300°.

5. *Mechanical sensitiveness.* (*a*) Falling weight. As in I 6 (*a*).

(*b*) Friction in mortar. As in I 6 (*b*). The standard powder gives no perceptible reaction.

(A) VII. *Dynamite and similar Explosives*

As standards of comparison *blasting gelatine* and *kieselguhr dynamite* are used, of the composition:

Blasting Gelatine	
Nitro-glycerine	93 per cent.
Collodion cotton	7 ,,

Kieselguhr Dynamite	
Nitro-glycerine	75 per cent.
Kieselguhr	25 ,,

The tests consist of:

1. Chemical analysis.
2. Behaviour to litmus paper.
3. Exposure to high temperature.
4. Shaking test.
5. Behaviour on ignition.
6. Mechanical sensitiveness.

1. *Chemical analysis.* Quantitative determination of nitro-glycerine, dinitro glycerine, chlorinated nitro-glycerine, nitro-cellulose, saltpetre, etc.

2. *Behaviour to litmus paper.* As in I 2. Nitro-glycerine explosives containing ammonium nitrate react slightly acid, like donarite.

3. *Warm storage* (at various temperatures). (*a*) Complete cartridges are to be kept for five days at 30°. No nitro-glycerine must sweat out, and after cooling the cartridges must be unchanged.

(*b*) Complete cartridges are to be kept for forty-eight hours at 75°. No red fumes must appear.

4. *Shaking test.* As in I 4.

5. *Behaviour on ignition.* (*a*) With safety fuse. As in I 5 (*a*). Gelatinized

explosives are cut into small cubes before being put into the test-tube. Guhr dynamite ignites and burns without explosion; blasting gelatine nearly always ignites and burns vigorously without explosion.

(*b*) In red-hot iron basin. As in I 5 (*b*). The standard explosives burn without explosion.

(*c*) In metal bath. As in I 5 (*c*). Guhr dynamite ignites at about 207°–215°, blasting gelatine at about 207°–211°.

(*d*) In wood fire. As in I 5 (*d*). Guhr dynamite ignites and may explode; blasting gelatine detonates.

6. *Mechanical sensitiveness.* (*a*) Falling weight. As in I 6 (*a*).

(*b*) 0·05 g. of the substance is rubbed in an unglazed porcelain mortar with a wooden pestle. The standard explosives do not explode.

B. Propellents

I and II. *Gelatinized Smokeless Powders free from and containing Nitro-glycerine*

The tests consist of:

1. Tests of the materials used in the manufacture of the powder, viz.:

(*a*) The *nitro-cellulose*. It must be of the best quality and pass the following stability tests:

(*α*) The nitro-cellulose must not give off more than 3 c.c. of nitric oxide per g. in two hours in the Bergmann and Junk test (*see* p. 667).

(*β*) The temperature of ignition must be above 180° C. as determined by the method given in A IV 1 (*b*).

(*b*) The *nitro-glycerine* must be of the best quality, it must be quite free from acid:

(*α*) Behaviour to litmus paper. 1 c.c. is shaken with 3 c.c. of distilled water and tested with sensitive blue litmus paper, which must not be coloured red.

(*β*) With zinc iodide-starch paper at 80°. 1 g. of the nitro-glycerine is to be tested. There must be no violet coloration of the test paper within ten minutes.

2. The *finished powder*. If it is to be classified in Group I, it must be gelatinized and satisfy the following conditions:

(*a*) Stability test. 1 g. of powder is placed in a thick glass tube 350 mm. long and 19·5 to 20 mm. external diameter, and this is heated to 130° to 132° C. for nitro-cellulose powder, or 120° C. for nitro-glycerine powder. The heating is carried out in the Bergmann and Junk apparatus (*see* p. 667), with the alteration that the tube is closed with a cork instead of with the bulb absorber. The time is observed when light yellowish-red fumes appear. With a nitro-cellulose powder they must not be visible before one hour has elapsed at 132°, or with nitro-glycerine powder before one and a half hours at 120°.

(*b*) Ignition point. As in A IV 1 (*b*). The powder is to be tested as far as possible in the form in which it is to be used: it must not be ground. Nitro-cellulose powder must not ignite below 170°, or nitro-glycerine powder below 160° C.

(*c*) Trauzl lead block test. To be carried out according to the method laid down at the Fifth International Congress of Applied Chemistry (*see* p. 469). As a standard of comparison, a nitro-glycerine powder is used made up into cubes with edges 2 mm. long, and consisting of 60 per cent. nitro-cellulose (12 per cent. nitrogen) and

40 per cent. nitro-glycerine. 10 g. fired with an electric detonator containing a charge of 0·54 g. must not form a cavity more than 10 per cent. larger than that formed by the standard explosive under the same conditions.

(B) III. *Black Powder*

There are no special tests for black powder used as a propellent.

C. OTHER EXPLOSIVES

When submitted in the dry state to the following tests they must not show themselves more dangerous than powdered pure picric acid (m.p. not less than 120° C.):

1. *Mechanical sensitiveness.* 0·05 g. is wrapped in tinfoil, laid on a block of brass resting on a stone foundation. A sharp-edged iron rod with an under surface of 1 sq. cm. is placed on it, and five hard blows are given with an iron hammer weighing at least 1 kg. This test is carried out five times.
2. *Behaviour on ignition.* As in A I 5 (*a*) and (*b*).

APPENDIX II

THERMO-CHEMICAL TABLES

Heats of formation, Oxygen compounds of non-metals: Other non-metallic inorganic compounds, Ammonia and its compounds, Compounds of metals: Fulminates and azides: Heats of formation and combustion of organic compounds, Hydrocarbons, Alcohols, solvents, etc., Carbohydrates, Aliphatic nitrates and nitro-compounds, aromatic nitro-compounds, etc.: Latent heats: Specific heats of solids

The two main authorities on heats of reaction are Berthelot and Thomsen, who have both published fairly comprehensive works on the subject, largely based on their own experiments; but where the actual determinations have been made by others, the results have been brought into general accordance with those of one or other of the authorities mentioned. The various figures being largely interdependent, it is always best, if possible, to adhere to one set of figures or the other, otherwise considerable errors may be introduced. For instance, Thomsen's figures for the heats of formation of carbon compounds are based on the supposition that they are formed from a porous amorphous form of carbon, which was found by Favre and Silbermann to evolve 96·96 calories when burnt to dioxide; Berthelot's figures, on the other hand, are calculated from the heat of oxidation of diamond, which is nearly 3 calories less.

In the following Tables only those substances are mentioned which are most likely to occur in calculations connected with explosives.

The Tables are made out on the assumption that all reactions take place under a constant pressure of one atmosphere. For explosive reactions taking place in a bomb at constant volume, it is therefore necessary to introduce a correction for the work that would be done by the gases in expanding to atmospheric pressure. This is equal to 0·00198 T.: hence at 18°, 0·58 calorie for every mol. of additional gas generated in the reaction, should be added on to the heat calculated for constant pressure.

The heats of formation are in all cases from the elements and are expressed in large calories per gramme-mol.

In the last column are also given the heats of solution (S) of those products of explosion that are liable to be dissolved by the water formed. Where these have a negative value, it means that the solution produces a fall of temperature. In concentrated solutions, however, the quantities of heat evolved or absorbed are somewhat less. In many cases the quantity of water formed is insufficient for complete solution.

HEATS OF FORMATION

Substance	Formula	Molecular Weight	Heat of Formation		Remarks
			Thomsen	Berthelot	
OXYGEN COMPOUNDS OF NON-METALS					
Ozone	O_3	48	− 34·2	—	gas
Water	H_2O	18	68·36	69·0	liquid
,,	,,	18	57·93	58·1	gas
Carbon monoxide	CO	28	29·0	26·1	,,
,, dioxide	CO_2	44	96·96	94·3	,,
Sulphur dioxide	SO_2	64	71·1	69·3	gas, rhombic S
,, trioxide	SO_3	80	103·2	—	liquid
,, ,,	,,	80	—	103·7	solid
Sulphuric acid	H_2SO_4	98	210·8	210·1	dissolved
Nitrous oxide	N_2O	44	− 17·7	− 20·6	gas
Nitric oxide	NO	30	− 21·6	− 21·6	,,
Nitrogen trioxide	N_2O_3	76	—	− 21·4	,,
,, peroxide	N_2O_4	92	− 2·6	− 1·7	,,
,, ,,	NO_2	46	− 8·1	− 7·6	,, at 150°
Nitric acid	HNO_3	63	—	34·4	,,
,, ,,	,,	63	41·5	41·6	liquid
,, ,,	,,	63	49·1	48·8	dissolved
Chlorine monoxide	Cl_2O	87	− 17·9	− 15·1	gas
Perchloric acid	$HClO_4$	100·5	—	18·8	liquid (S, 10·3)
Antimonious acid	H_3SbO_3	171·2	167·4	—	solid
Antimonic acid	H_3SbO_4	187·2	228·8	—	,,
OTHER NON-METALLIC INORGANIC COMPOUNDS					
Hydrazoic acid (azoimide)	N_3H	43	—	58·2	dissolved
Ammonium azide	N_4H_4	60	—	− 19·0	solid
Nitrogen sulphide	N_4S_4	184	—	− 127·6	,,
,, selenide	N_4Se_4	372	—	− 169·2	,,
,, chloride	NCl_3	120·5	—	− 38·0	liquid
Antimony sulphide	Sb_2S_3	336·6	—	34·4	
Cyanogen	C_2N_2	52	− 65·7	− 73·8	gas
Hydrocyanic acid	HCN	27	—	− 24·4	dissolved
Cyanic acid	$HCNO$	43		37·0	,,
Cyanamide	NH_2CN	42	—	− 8·2	
Hydrochloric acid	HCl	36·5	22·0	22·0	gas
,, ,,	,,	36·5	39·3	39·4	dissolved
Hydrogen sulphide	H_2S	34	2·7	2·3	gas

HEATS OF FORMATION—*continued*

Substance	Formula	Molecular Weight	Heat of Formation		Remarks
			Thomsen	Berthelot	
AMMONIA AND ITS COMPOUNDS					
Ammonia	NH_3	17	11·9	12·2	gas [1]
,, ...	,,	17	20·3	21·0	dissolved
Ammonium chloride .	NH_4Cl	53·5	75·8	76·8	
,, perchlorate .	NH_4ClO_4	117·5	—	79·7	solid
,, nitrate .	NH_4NO_3	80	88·05	88·6	
,, carbonate .	$(NH_4)_2CO_3$	96	—	221·6	dissolved
,, bicarbonate .	$NH_4.HCO_3$	79	—	205·3	solid (S. — 6·3)
COMPOUNDS OF METALS					
Sodium chloride . .	$NaCl$	58·5	97·7	97·9	solid (S. — 1·2)
,, chlorate . .	$NaClO_3$	106·5	86·7	84·8	,,
,, perchlorate .	$NaClO_4$	122·5	—	100·3	,,
,, nitrate . .	$NaNO_3$	85	111·25	110·7	,,
,, carbonate . .	Na_2CO_3	106	272·6	270·8	,, (S. + 5·6)
,, bicarbonate .	$NaHCO_3$	84	229·3	227·0	,, (S. — 4·3)
,, sulphide . .	Na_2S	78	—	89·3	,, (S. + 15·0)
,, tetrasulphide .	Na_2S_4	174	—	99·0	,, (S. + 9·8)
,, sulphate . .	Na_2SO_4	142	328·6	328·1	,, (S. + 0·5)
Potassium chloride .	KCl	74·6	105·6	105·7	solid (S. — 4·4)
,, chlorate .	$KClO_3$	122·6	95·8	93·8	,,
,, perchlorate .	$KClO_4$	138·6	—	113·5	,,
,, sulphide .	K_2S	110·3	—	103·5	,, (S. + 10·0)
,, tetrasulphide .	K_2S_4	206·4	—	118·6	,, (S. + 1·4)
,, cyanide .	KCN	65·2	32·5	30·1	,, (S. — 3·0)
,, cyanate .	$KCNO$	81·2	—	102·5	,, (S. — 5·2)
,, sulphocyanide	$KCNS$	97·3	—	49·8	,, (S. — 6·1)
,, ferrocyanide .	$K_4Fe(CN)_6$	368·3	—	137·2	,,
,, sulphate .	K_2SO_4	174·2	344·6	344·3	,, (S. — 6·3)
,, nitrate . .	KNO_3	101·1	119·5	119·0	,,
,, carbonate .	K_2CO_3	138·2	281·1	278·8	,, (S. + 6·5)
,, bicarbonate .	$KHCO_3$	100·1	—	233·3	,, (S. — 5·3)
Calcium nitrate . .	$Ca(NO_3)_2$	164	216·8	202·0	solid
,, carbonate . .	$CaCO_3$	100	284·5	270·5	,,

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[1] According to Haber 11·0 at 18°.

HEATS OF FORMATION—*continued*

Substance	Formula	Molecular Weight	Heat of Formation		Remarks
			Thomsen	Berthelot	
COMPOUNDS OF METALS—*continued*					
Barium chlorate . .	$Ba(ClO_3)_2$	304·3	—	171·2	solid
,, perchlorate .	$Ba(ClO_4)_2$	336·3	—	201·4	,,
,, nitrate . .	$Ba(NO_3)_2$	261·4	228·4	227·2	,,
,, carbonate . .	$BaCO_3$	197·4	285·6	282·5	amorphous
Magnesium oxide . .	MgO	40·3	—	143·3	solid
,, hydroxide .	$Mg(OH)_2$	58·3	217·3	217·8	,,
,, carbonate .	$MgCO_3$	84·3	—	266·6	,,
Aluminium oxide . .	Al_2O_3	102·2	—	380·2	,,
,, hydroxide .	$Al(OH)_3$	78·1	194·5	196·5	,,
,, sulphide .	Al_2S_3	150	—	126·4	,,
Manganese oxide . .	MnO	71	—	90·8	,,
,, ,, . .	Mn_3O_4	229	—	324·9	,,
,, dioxide .	MnO_2	87	—	126·0	,,
Potassium permanganate	$KMnO_4$	158	194·8	200·0	,,
Iron oxide . . .	FeO	72	—	65·7	,,
,, ,, ...	Fe_3O_4	232	—	270·8	,,
Cupric oxide. . .	CuO	79·6	37·2	—	,,
Cuprous oxide . .	Cu_2O	143·2	40·8	43·8	,,
Lead oxide . . .	PbO	223	50·3	—	,,
,, nitrate . .	$Pb(NO_3)_2$	331	105·5	—	,,

The heats of formation of chromium compounds from metallic chromium have not been determined, but Thomsen gives the heat of formation of potassium bichromate from the sesquioxide, potassium and oxygen: K_2, Cr_2O_3, O_4, 15·0 Cals.

Substance	Formula	Molecular Weight	Heat of Formation	Authority
Mercuric fulminate . .	$Hg(OCN)_2$	284·6	— 62·9	Berthelot
,, ,, . .	,,	284·6	— 60·8	Martin
Silver ,, . .	$AgOCN$	149·9	— 44·4	,,
Cadmium ,, . .	$Cd(OCN)_2$	196·4	— 47·8	,,
Mercurous azide . .	Hg_2N_6	484·6	— 144·8	Berthelot & Vieille
,, ,, . .	,,	484·6	— 129·0	Martin
Silver ,, . .	AgN_3	149·9	— 67·8	,,
Lead ,, . .	PbN_6	291·3	— 105·9	,,
Cadmium ,, . .	CdN_6	196·5	— 109·6	,,

HEATS OF FORMATION AND COMBUSTION OF ORGANIC COMPOUNDS

As the heats of combustion have in most cases been determined directly, they are not affected by assumptions as to the quantities of heat liberated in other reactions; but this, of course, does not apply to the heats of formation, which are calculated from the heats of combustion by subtracting the heats of formation of carbon dioxide, water, and any other substances that may be formed.

Thomsen determined the heats of combustion by burning the vapour of the substance with oxygen in a special calorimeter. He could, therefore, only experiment on substances that are volatile: his results are calculated for the substance in the state of gas at 18° burning under constant pressure. Many of the results of Berthelot and others have been obtained in a bomb calorimeter with oxygen under pressure, but the results have been corrected to constant pressure, and refer to the substance in the form in which it exists at the ordinary temperature and pressure. In order to facilitate comparison the heat of volatilization (v) has been given in some instances.

Substance	Formula	Molecular Weight	Heat of Formation		Heat of Combustion		Remarks
			Thomsen	Berthelot	Thomsen	Berthelot	
			HYDROCARBONS				
Methane .	CH_4	16	21·75	18·9	211·9	213·5	
Ethane .	C_2H_6	30	28·6	23·3	370·4	372·3	
Propane .	C_3H_8	44	35·1	30·5	529·2	528·4	
Ethylene .	C_2H_4	28	— 2·7	— 14·6	333·3	341·1	
Acetylene .	C_2H_2	26	— 47·8	— 58·1	310·0	315·7	
Benzene (vapour) .	C_6H_6	78	— 12·5	— 4·1	799·9	785·1	v. 7·3 at 80°
Toluene .	C_7H_8	92	— 3·5	+ 2·3	955·7	933·8	v. 8·0 at 111°
Naphthalene.	$C_{10}H_8$	128	—	— 22·8	1233·6	1241·8	solid
			ALCOHOLS, SOLVENTS, ETC.				
Methyl alcohol	CH_4O	32	51·45	61·4	182·2	170·6	v. 9·2 at 0°
Ethyl alcohol	C_2H_6O	46	58·5	69·9	340·5	325·7	v. 10·9 at 0°
Amyl alcohol	$C_5H_{12}O$	88	74·9	91·6	820·1	793·9	v. 10·7 at 121°
Glycerine .	$C_3H_8O_3$	92	—	160·9	—	397·1	
Ether . .	$C_4H_{10}O$	74	70·0	70·5	956·6	651·7	v. 6·6 at 15°
Formaldehyde	CH_2O	30	—	25·4	—	—	gas (Delépine)
Acetaldehyde	C_2H_4O	44	48·7	47·5	281·9	279·1	v. 6·0
Acetone .	C_3H_6O	58	58·7	63·0	437·2	426·9	v. 8·1 at 0°

Substance	Formula	Molecular Weight	Heat of Formation		Heat of Combustion		Remarks
			Thomsen	Berthelot	Thomsen	Berthelot	
ALCOHOLS, SOLVENTS, ETC.—*continued*							
Camphor (*a*).	$C_{10}H_{16}O$	152	—	77·7	—	1414·3	
Ethyl acetate	$C_4H_8O_2$	88	114·7	—	546·6		
Phenol.	C_6H_6O	94	—	36·8	—	736·0	
Cresol (m)	C_7H_8O	108	—	53·0	—	881·0	liquid
Zinc ethyl	ZnC_4H_{10}	123	—	2·8	—	—	,,
Aniline	$C_6H_5NH_2$	93	− 17·4	− 11·2	838·5	818·5	v. 9·7 at 183°
Diphenylamine	$(C_6H_5)_2NH$	169	—	− 26·8	—	1537·9	Mean figures
Urea	CH_4ON_2	60	—	80·8	—	151·5	
Guanidine	CH_5N_3	59	—	19·2	—	247·6	
Pentaerythritol	$C(CH_2OH)_4$	136	—	223·6	—	661·9	Stohmann
Resorcinol	$C_6H_4(OH)_2$	110	—	89·1	—	683·7	Mean figures
Anisol	$C_6H_5OCH_3$	108	—	32·2	—	903·9	,, ,,
Phenetol	$C_6H_5OC_2H_5$	122	—	41·5	—	1057·9	,, ,,
Benzoic acid	C_6H_5COOH	122	—	95·6	—	771·5	,, ,,

CARBOHYDRATES

Substance	Formula	Molecular Weight	Heat of Formation Berthelot	Heat of Combustion Berthelot	Remarks
Glucose	$C_6H_{12}O_6$	180	302·6	677·2	
Cane sugar	$C_{12}H_{22}O_{11}$	342	535·6	1355·0	
Dextrine	$C_6H_{10}O_5$	162	243·6	667·2	
Starch	,,	162	225·9	684·9	
Cellulose	,,	162	230·4	681·8	
Wood-meal	$C_{50}H_{72}O_{33}$	1200	1500	5700	
Charcoal	per kg.	—	—	8500 8700	

The figures for wood-meal have been calculated from the mean of the results that have been published, using Berthelot's heat of formation of carbon dioxide. The figures for the other carbohydrates are due to Berthelot and his collaborators.

Substance	Formula	Molecular Weight	Heat of Formation	Heat of Combustion	Authority
		ALIPHATIC NITRATES AND NITRO-COMPOUNDS			
Tetranitro-methane	$C(NO_2)_4$	196	4·7	89·6	Berger
Glycerine mononitrate	$C_3H_7NO_5$	137	139·2	385·2	Will
.. dinitrate α (dry)	$C_3H_6N_2O_7$	182	109·9	380·0	,,
.. .. α (crys.)	$C_3H_6N_2O_7\frac{1}{2}H_2O$	191	—	373·3	,,
.. .. β	$C_3H_6N_2O_7$	182	115·9	374·0	..
.. trinitrate	$C_3H_5N_3O_9$	227	98·0	356·5	Berthelot
.. ..	,,	227	94·5	360·5	Sarrau & Vieille
.. ..	..	227	99·0	356·4	Will
Mannitol hexanitrate	$C_6H_8(NO_3)_6$	452	163·3	678·5	Sarrau & Vieille
,, ,,	..	452	156·1	—	Berthelot
Pentaerythritol tetranitrate	$C(CH_2NO_3)_4$	316	115·5	—	Koehler
Gun-cotton	$C_{24}H_{29}N_{11}O_{42}$	1143	633	—	Sarrau & Vieille
,,	,,	1143	624	—	Berthelot
..	,,	1 kg.	546	—	,,
..	13 per cent. N	1 kg.	544	—	various
Collodion cotton	$C_{24}H_{31}N_9O_{38}$	1053	696	—	Berthelot
.. ,,	,,	1 kg.	661	—	,,
,, ..	$C_{24}H_{32}N_8O_{36}$	1008	706	—	..
Guanidine nitrate	$CH_6N_4O_3$	122	93·5	207·8	Matignon
Nitro-guanidine	$CH_4N_4O_2$	104	22·0	210·3	,,
		AROMATIC NITRO-COMPOUNDS, ETC.			
Nitro-benzene	$C_6H_5NO_2$	123	4·2	—	Berthelot (liquid)
,,	,,	123	3·9	734·6	Swarts
Dinitro-benzene (o)	$C_6H_4(NO_2)_2$	168	0·3	703·5	Berthelot and Matignon
.. (m)	,,	168	6·8	697·0	
.. (p)	..	168	8·4	695·4	
.. (m)	..	168	8·6	695·1	Swarts
Trinitro-benzene 1 : 3 : 5	$C_6H_3(NO_2)_3$	213	4·5	—	Koehler
.. 1 : 2 : 4	..	213	− 9·2	—	..
Nitro-toluene (m)	$C_7H_7NO_2$	137	11·0	889·6	Swarts
Trinitro-toluene 2 : 4 : 6	$C_7H_5(NO_2)_3$	227	7·7	—	from Bichel's figures
.. (all isomers)	..	227	1·8	830·8	Will
.. 2 : 4 : 6	..	227	5·9	—	Koehler
Nitro-naphthalene	$C_{10}H_7NO_2$	173	− 14·7	—	Sarrau
Nitro-phenol (o)	$C_6H_4OH.NO_2$	139	50·1	688·2	Matignon (solid)
.. (o)	..	139	50·1	688·0	Swarts

Substance	Formula	Molecular Weight	Heat of Formation	Heat of Combustion	Authority
AROMATIC NITRO-COMPOUNDS, ETC.—*continued*					
Nitro-phenol (m) .	$C_6H_4OH.NO_2$	139	53·7	684·4	Swarts
,, (p) .	,,	139	49·2	689·1	Matignon
,, (p) .	,,	139	50·0	688·2	Swarts
Picric acid . .	$C_6H_2OH(NO_2)_3$	229	50·9	618·4	Sarrau & Vieille
,, ,, . .	,,	229	50·2	—	Koehler
Ammonium picrate .	$C_6H_6N_4O_7$	246	81·8	691·0	Sarrau & Vieille
Potassium picrate .	$C_6H_2OK(NO_2)_3$	267	119·6	619·7	,, ,,
Trinitro-cresol . .	$C_7H_4OH(NO_2)_3$	243	54·1	—	Koehler
Trinitro-resorcinol (styphnic acid)	$C_6H(OH)_2(NO_2)_3$	245	109·3	—	,,
Nitro-phenetol (o) .	$C_6H_4OC_2H_5.NO_2$	167	43·4	1021·2	Swarts (liquid)
,, (m) .	,,	167	55·6	1009·2	,, (solid)
,, (p) .	,,	167	58·4	1006·0	,, ,,
Nitro-benzoic acid (o)	$C_6H_4COOH.NO_2$	167	102·2	730·4	Matignon and Deligny
,, ,, (m)	,,	167	105·6	727·0	
,, ,, (p)	,,	167	103·8	728·8	
Nitro-aniline (o) .	$C_6H_4NH_2.NO_2$	138	6·9	765·9	Swarts
,, (m) .	,,	138	6·5	766·3	,,
,, (p) .	,,	138	12·3	760·2	,,
Trinitro-aniline 2 : 4 : 6 (picramide)	$C_6H_2NH_2(NO_2)_3$	228	15·2	—	Koehler
Tetranitro-methyl-aniline (tetryl)	$C_7H_5N_5O_8$	287	− 40·8	—	,,
Diphenylamine nitrosamine	$(C_6H_5)_2N.NO$	198	− 56·4	1533·0	Matignon and Deligny
p-nitrosophenyl-aniline	$C_6H_4(NO)NHC_6H_5$	198	− 50·8	1527·4	
Diazo-benzene nitrate	$C_6H_5NNNO_3$	167	− 44·6	782·9	Berthelot & Vieille

For nitro-aromatic compounds Berthelot gave the rule that the introduction of a nitro-group increases the heat of formation by 9 calories. The knowledge we now possess shows that this value is too high in many cases. The heats of formation of the nitro-derivatives of the aromatic hydrocarbons are, like those of the parent substances, very small, and may be either positive or negative, the value depending more upon the distribution of the nitro-groups than upon their number. For a compound of this class, the heat of formation of which has not been determined, no great error will be introduced if it be assumed that it is 0 (C, diamond).

LATENT HEATS (Cals. per g. Atom)

Substance	M.p.	Heat of Fusion	Temperature of Vapour	Heat of Vaporization
Lead	326°	1·1		
Iron	1000°	1·9		
Sulphur . . .	115°	0·3	316°	11·6
Tin	228°	1·6		
Mercury . . .	– 39°	0·6	358°	13·6
Aluminium . . .	625°	6·5[1]		

SPECIFIC HEATS OF SOLIDS
(Heat in small calories required to raise temperature 1° C.)

Substance	Symbol	Temperature	Specific Heat	Molecular Heat	Authority
Aluminium . .	Al	15° 185°	·219	5·94	Tilden
		10°	·222	6·01	Richards
		600°	·282	7·65	,,
Lead . . .	Pb	15°	·0299	6·20	Naccari
		200°	·0324	6·71	,,
		300°	·0338	7·00	,,
Iron (steel) . .	Fe	0°–18°	·1066	5·95	Hill
		20°–100°	·1178	6·63	,,
		500°	·1764	9·85	Pionchon
		700°	·3243	18·1	,,
		720°–1000°	·218	12·2	,,
		1000°–1200°	·199	11·1	,,
Carbon (charcoal) .	C	0°–24°	·1653	1·99	Weber
		0°–224°	·2385	2·86	,,
(graphite) .		10·8°	·1604	1·92	,,
		138°	·2542	3·06	,,
		977°	·4670	5·60	,,
		0°–2000°	·475	5·70	Violle
		0°–3000°	·535	6·32	,,
Copper	Cu	20° 100°	·0936	5·95	Schmitz
		900°	·1259	8·00	Richards
		780°–1000°	·118	7·51	Le Verrier

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[1] This is the total heat required to heat 27·1 g. of aluminium from 0° to 625° and melt it.

Specific Heats of Solids—*continued*

Substance	Symbol	Temperature	Specific Heat	Molecular Heat	Authority
Mercury . . .	Hg	0°	·0334	6·76	Naccari
		250°	·0321	6·44	,,
Sulphur . . .	S	17°–45°	·163	5·22	Kopp
(liquid) .		116°–136°	·2317	7·43	Classen
(viscous) .		160°–201°	·279	8·95	Dussy
		201°–233°	·331	10·6	,,
		233°–264°	·324	10·4	,,
Tin . . .	Sn	19°–99°	·0552	6·57	Voigt
		16°–197°	·0588	7·00	Spring
(liquid) . .		250°–350°	·0637	7·58	Person
		1100°	·0758	9·02	Pionchon
Aluminium oxide .	Al_2O_3	26°	·2003	20·5	Russell
Antimony oxide .	Sb_2O_3	18°–100°	·0927	26·5	Neumann
Lead oxide . .	PbO	22°–98°	·0512	11·4	Regnault
Iron oxide . .	Fe_3O_4	24°–99°	·1678	38·8	,,
Copper oxide . .	CuO	12°–98°	14·20	11·3	,,
Magnesium oxide .	MgO	24°–100°	·2439	9·63	,,
Quartz . . .	SiO_2	20°–50°	·186	11·2	Kopp
		0°	·1737	10·4	Pionchon
		350°	·2786	16·8	,,
		400°–1200°	·305	19.4	,,
Tin oxide . .	SnO_2	16°–98°	·0933	14·1	Regnault
Potassium chloride .	KCl	14°–99°	·1730	12·9	,,
Sodium chloride .	NaCl	15°–98	·2140	12·5	,,
Potassium sulphate .	K_2SO_4	15°–98°	·1901	33·1	,,
Sodium sulphate .	Na_2SO_4	17°–98°	·2312	32·8	,,
Potassium hyposulphite	$K_2S_2O_3$	20°–100°	·197	37·5	Pape

Specific Heats of Solids—*continued*

Substance	Symbol	Temperature	Specific Heat	Molecular Heat	Authority
Sodium hyposulphite	$Na_2S_2O_3$	25°–100°	·221	36·5	Pape
Barium carbonate .	$BaCO_3$	11°–99°	·1104	21·7	Regnault
Calcium carbonate (aragonite)	$CaCO_3$	16°–45°	·203	20·3	Kopp
		0°–100°	·2065	20·6	Lindner
		0°–200°	·2121	21·2	,,
		0°–300°	·2176	21·8	,,
Potassium carbonate	K_2CO_3	23°–99°	·2162	29·9	Regnault
Sodium carbonate .	Na_2CO_3	16°–98°	·2728	29·0	,,
Silicates . . .	—	0°–100°	·17–·21	—	Various

APPENDIX III

CONVERSION OF UNITS

Pressure

	Atmosphere	Kg./sq. cm.	Tons./sq. in.
1 atmosphere	1	1·033	·006562
1 kg. per sq. cm.	·9678	1	·006350
1 ton per sq. in.	152·4	157·5	1

Mechanical Equivalent of Heat

424 kilogramme-metres = 1 Calorie (large)

Temperature

$c = $ °C. $\qquad f = 1{\cdot}8\,c + 32.$

$f = $ °F. $\qquad c = {\cdot}555\,(f - 32).$

Length

1 inch	=	25·40 mm.	1 millimetre	=	·03937 in.
1 foot	=	30·48 cm.	1 centimetre	=	·03281 ft.
1 yard	=	·9144 m.	1 metre	=	1·084 yd.

Capacity

1 pint	=	·5679 litre.	1 litre	=	1·761 pint.
1 gallon	=	4·543 litre.	1 litre	=	·2201 gallon.

Weight

1 grain	=	·06480 g	1 gramme.	=	15·43 gr.
1 ounce (av.)		28·35 g.	1 gramme		·03527 oz.
1 pound (av.)		453·6 g.	1 kilogramme		2·205 lb.
1 ton		1016·0 kg.	1 metric ton		·984 ton.

1 gallon contains 10 lb. of water at 62° F.
1 litre contains 1 kg. of water at 4° C.

Hydrometers

Twaddell for liquids heavier than water:

$$d = 1 + 0{\cdot}005n$$

Baumé for liquids heavier than water:

German scale $d = \dfrac{144{\cdot}3}{144{\cdot}3 - n}$

American scale $d = \dfrac{145}{145 - n}$

Dutch scale $d = \dfrac{144}{144 - n}$

Baumé for liquids lighter than water:

Continental scale $d = \dfrac{146}{136 - n}$

American scale $d = \dfrac{140}{130 - n}$

where d is the density as compared with water and n the number of degrees on the hydrometer.

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